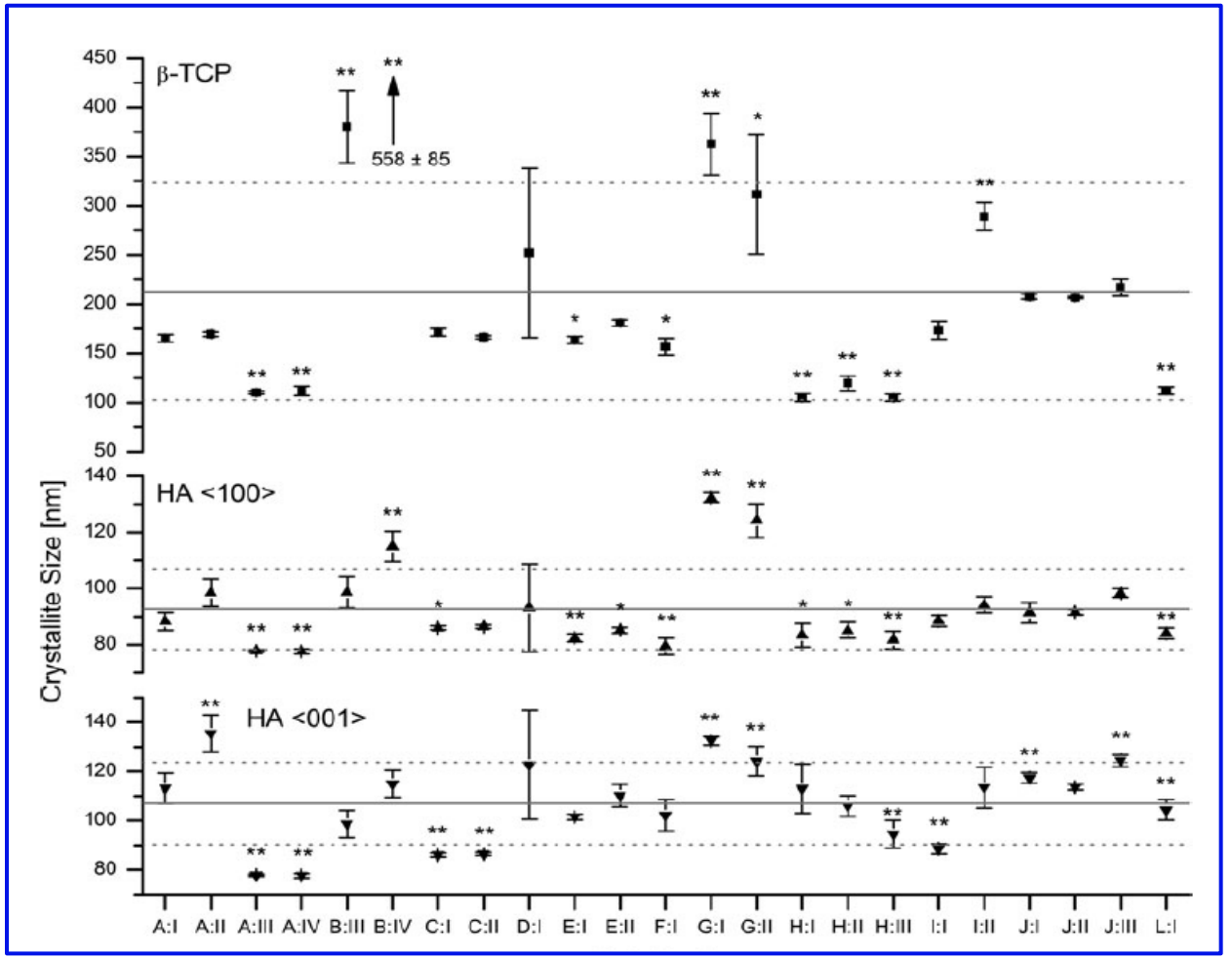
PSI

X-ray diffraction and scattering (WAXS) methods

MSE-674

Multidisciplinary approach to NPs characterization

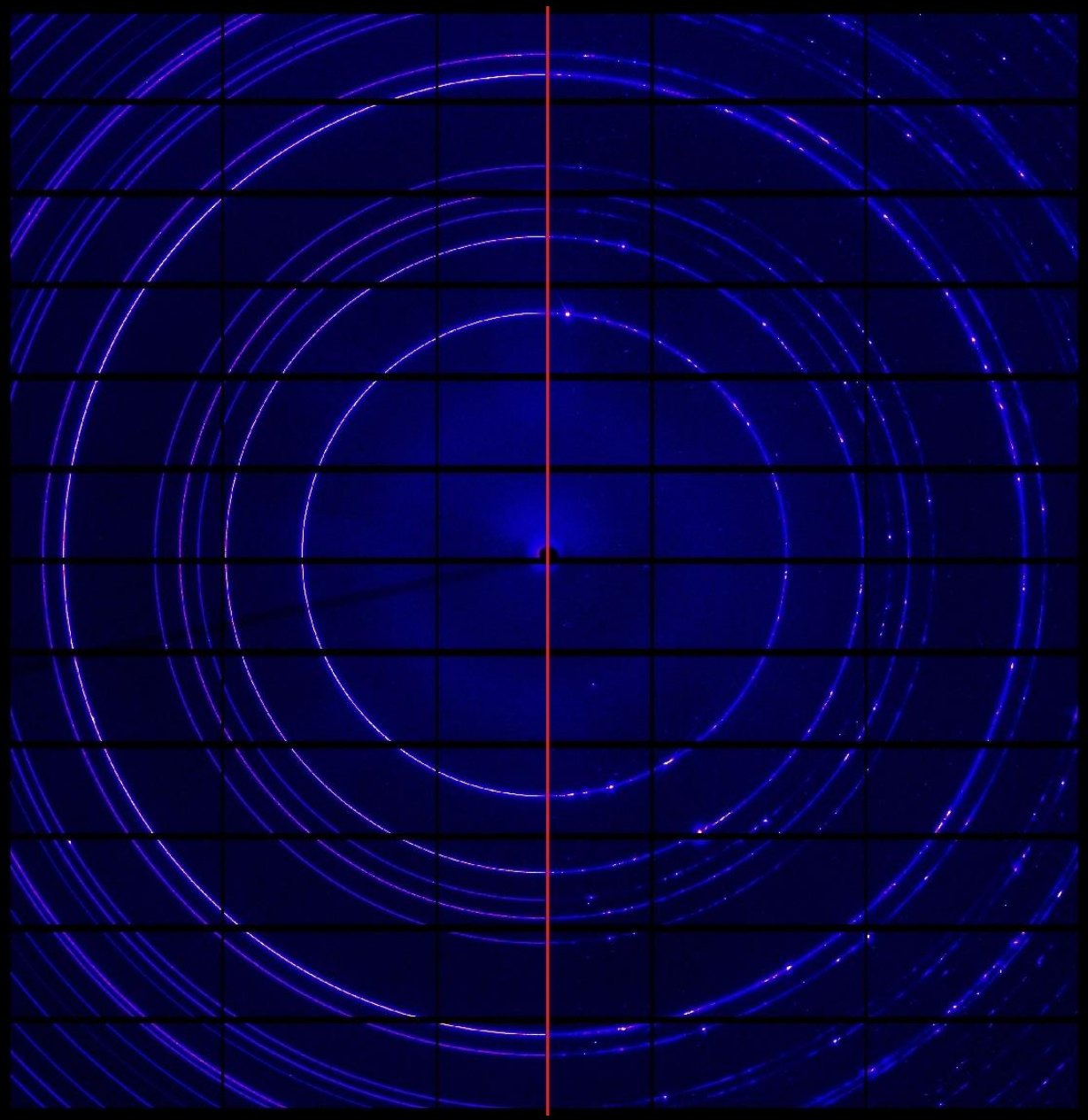


Nicola Casati

ADDAMS beamline, Advanced DiffrAction for Materials Science

Multidisciplinary approach to NPs characterization, January 2025

Outline



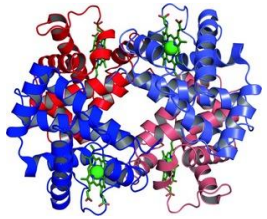
- Brief recap of XRD
- Instrumentation
- **Size** & Strain
- Some advanced stuff
- What's a Refinement?
- Play time

Diffraction for materials

Where are the atoms?

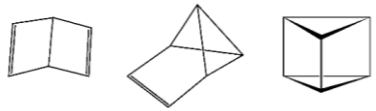
How are they linked?

Protein structure

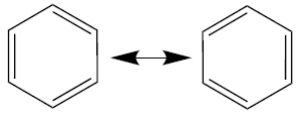


Activity

Molecules

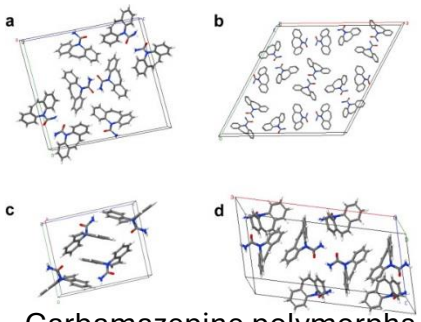


Dewar benzvalene prismane



Reactivity

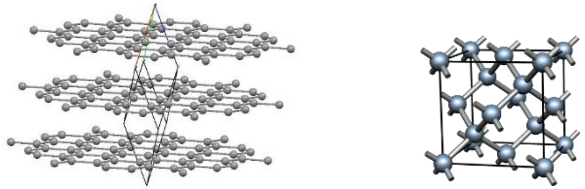
Pharmaceutical phases



Carbamazepine polymorphs

Bioavailability

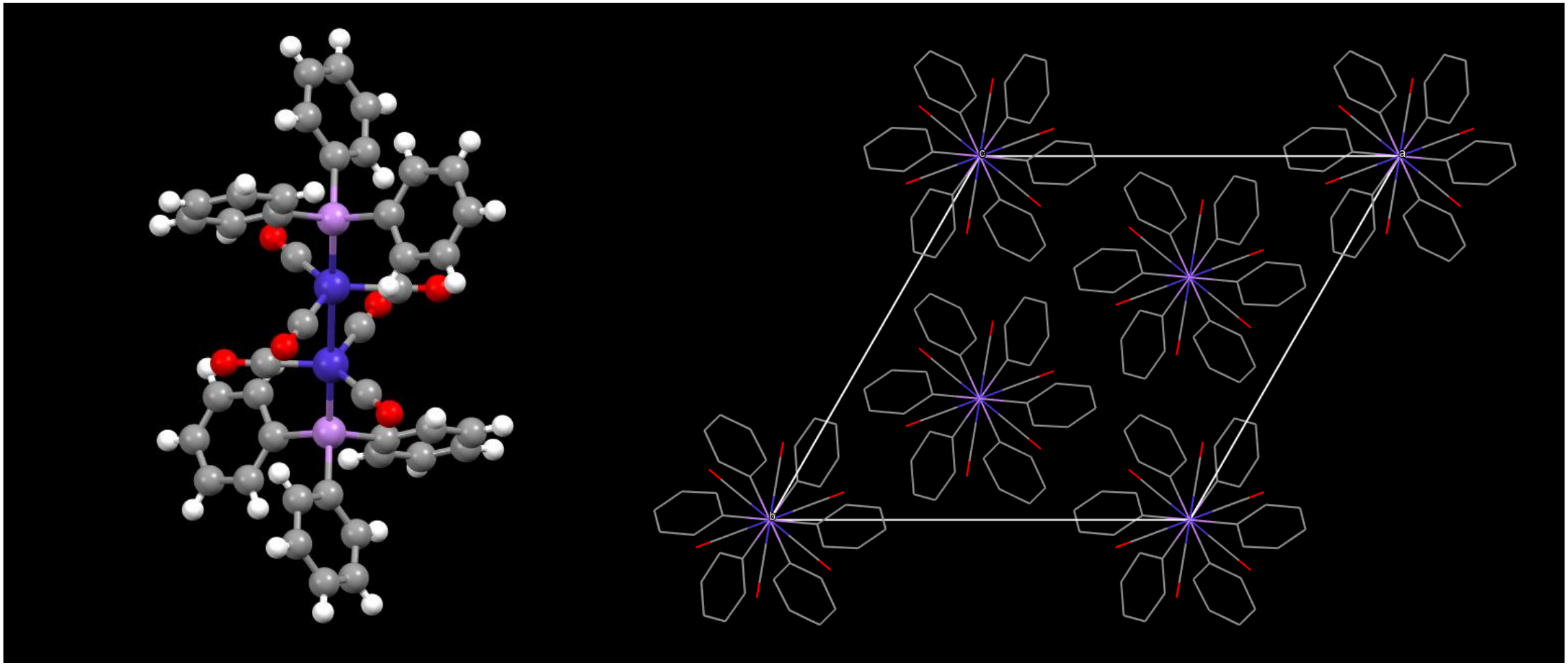
Materials



Graphite vs Diamond

Properties

What's a crystal structure?

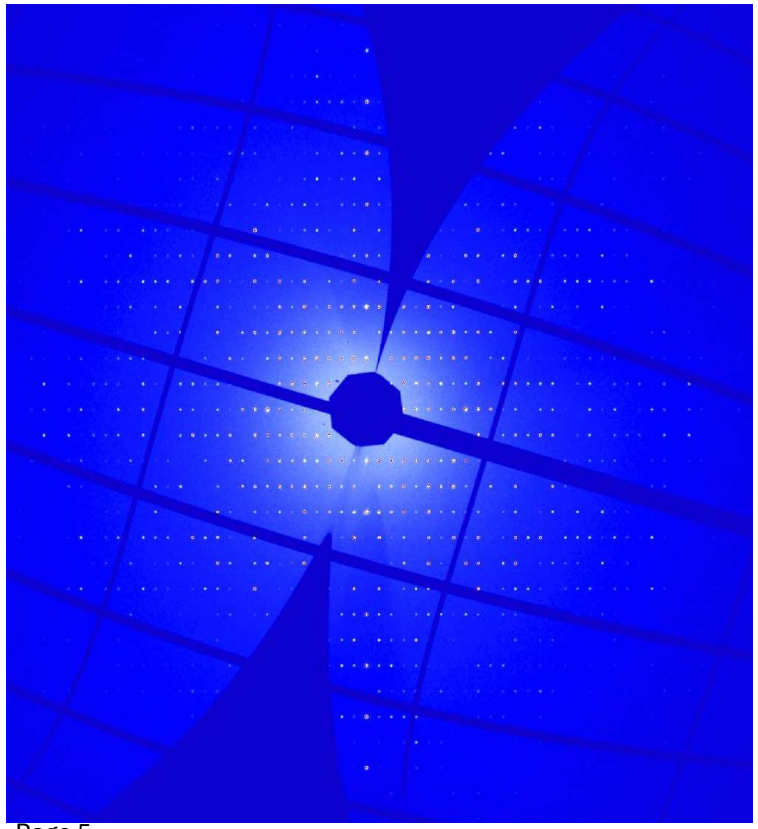


From structure to diffraction and back

PSI

Diffraction signal ⟷ CIF

(Crystallographic Information File)



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_symmetry_cell_setting              monoclinic
_symmetry_space_group_name_H-M      'P 21/n'
_symmetry_Int_Tables_number         14
_space_group_name_Hall              '-P 2yn'
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 1/2-x,1/2+y,1/2-z
3 -x,-y,-z
4 1/2+x,1/2-y,1/2+z
_cell_length_a                      9.097(1)
_cell_length_b                      12.764(1)
_cell_length_c                      9.822(1)
_cell_angle_alpha                   90
_cell_angle_beta                    94.69(1)
_cell_angle_gamma                   90
_cell_volume                        1136.65
_cell_formula_units_Z               4
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C -0.38703 0.00423 0.28159
C2 C -0.28602 -0.06814 0.23386
C3 C -0.19539 -0.04813 0.13133
C4 C -0.20615 0.03174 0.03190
C5 C -0.30673 0.11217 0.01310
C6 C -0.39942 0.14750 0.11176
C7 C -0.53656 0.19540 0.08539
```

Databases and programs (just hints)

Powder Diffraction File™	https://www.icdd.com/pdfsearch/
Cambridge Structure Database	http://www.ccdc.cam.ac.uk/
Inorganic Crystal Structure Database	http://www.fiz-karlsruhe.de/icsd.html
Crystalloghaphy Open Database	http://www.crystallography.net/
PDB (Protein DataBanck)	https://www.rcsb.org/

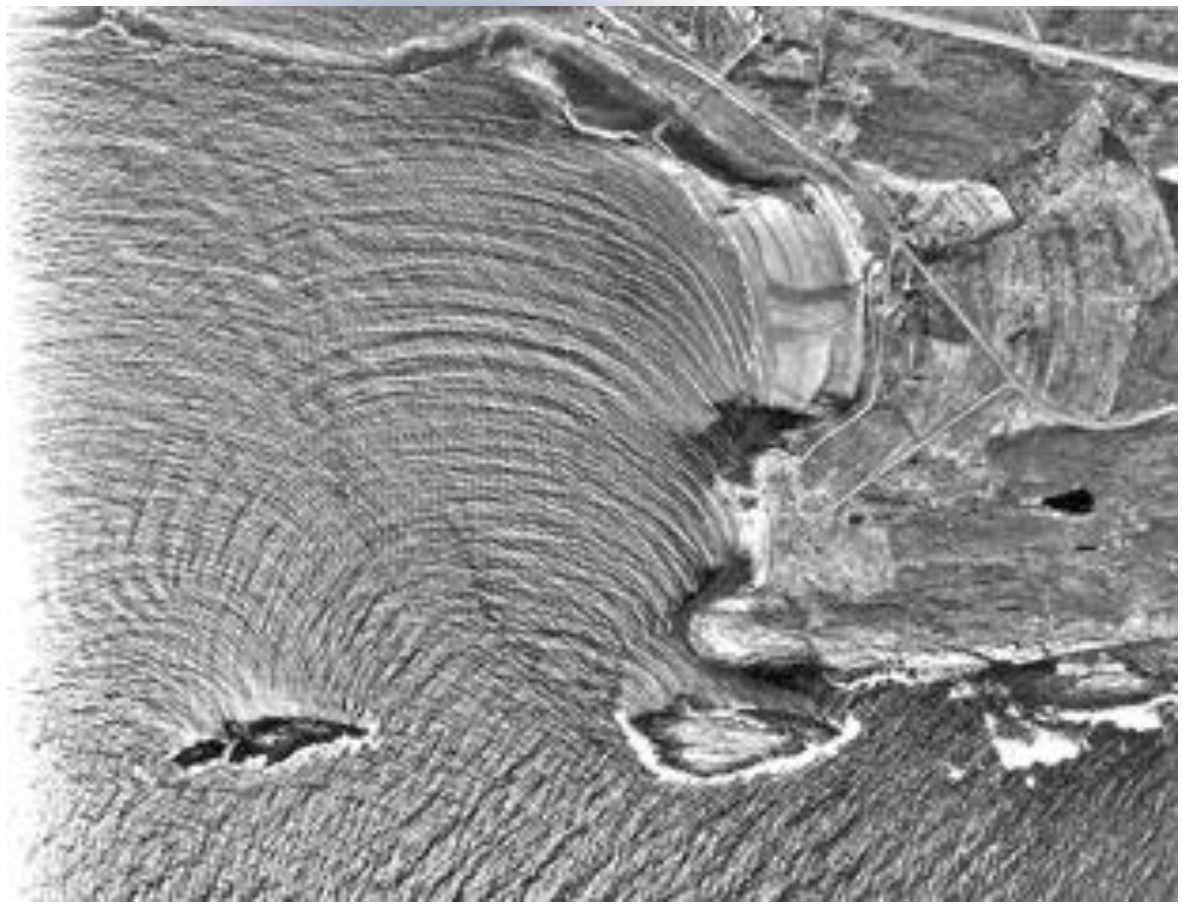
…. normally from single crystals (less than 1% from powders)

Topas	http://www.topas-academic.net/
GSAS-II	https://advancedphotonsource.github.io/GSAS-II-tutorials/
Fullprof	https://www.ill.eu/sites/fullprof/

Mercury	https://www.ccdc.cam.ac.uk/solutions/software/free-mercury/

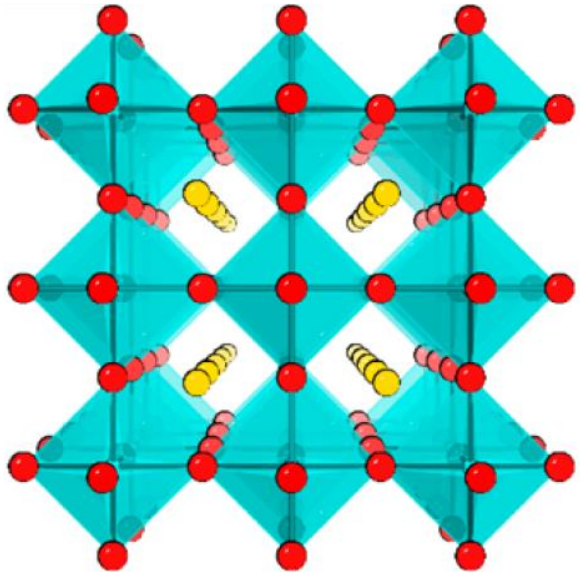
An Interferometric method

Interferometric: using the interference between waves (light) to obtain information (typically with the same length scale of the wavelength used)

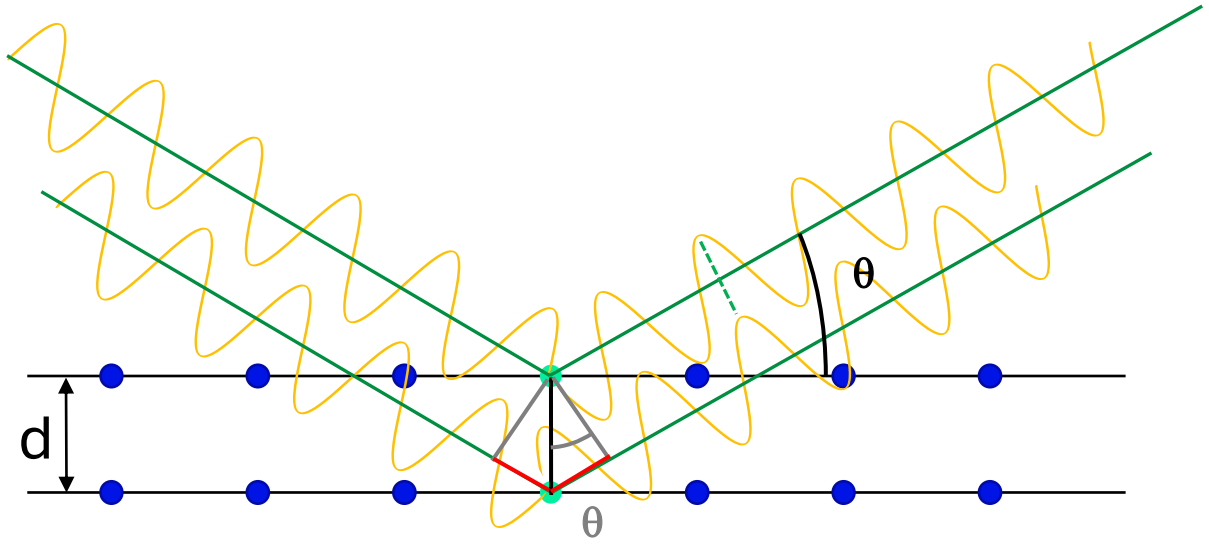


CRYSTALS

Ordered arrangement of atoms with periodic repetition in all directions (3D grating)



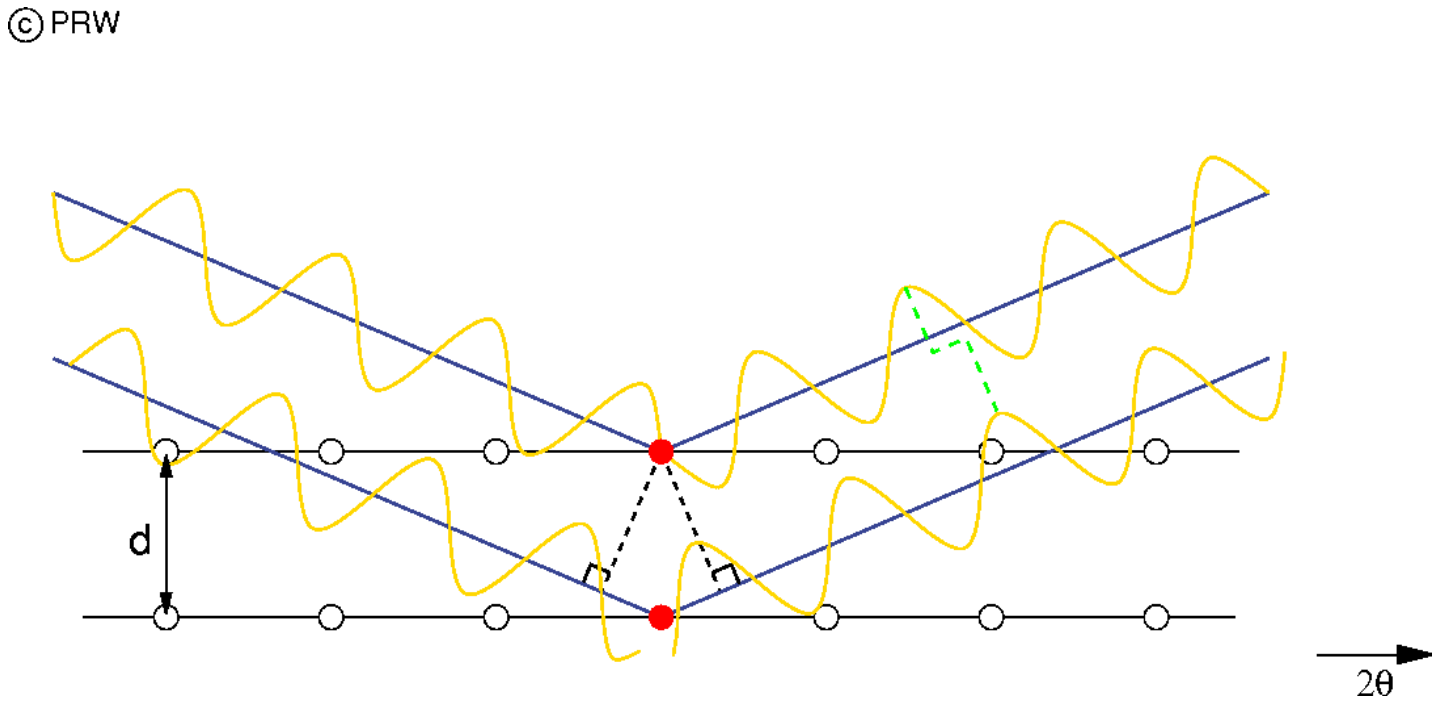
Scattering from a crystal



$n\lambda = 2\mathbf{d}\sin(\theta)$ Bragg's law

- What are the dots that scatter elastically the X-rays in crystals?
- X-rays are electromagnetic waves and they interact primarily with **electrons** (clouds)
- Different elements possess different Z, so scatter more or less strongly

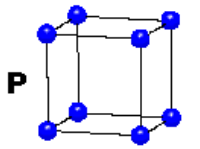
That equation ...



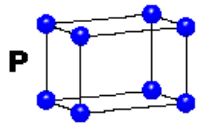
$$m\lambda = 2d \sin \theta$$

Indexing, Bravais lattice

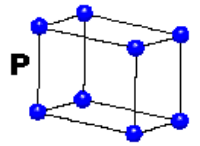
CUBIC
$a = b = c$
$\alpha = \beta = \gamma = 90°$



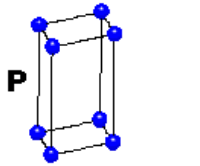
TETRAGONAL
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$



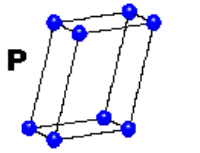
ORTHORHOMBIC
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$



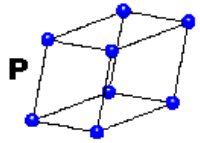
HEXAGONAL
$a = b \neq c$
$\alpha = \beta = 90°$
$\gamma = 120°$



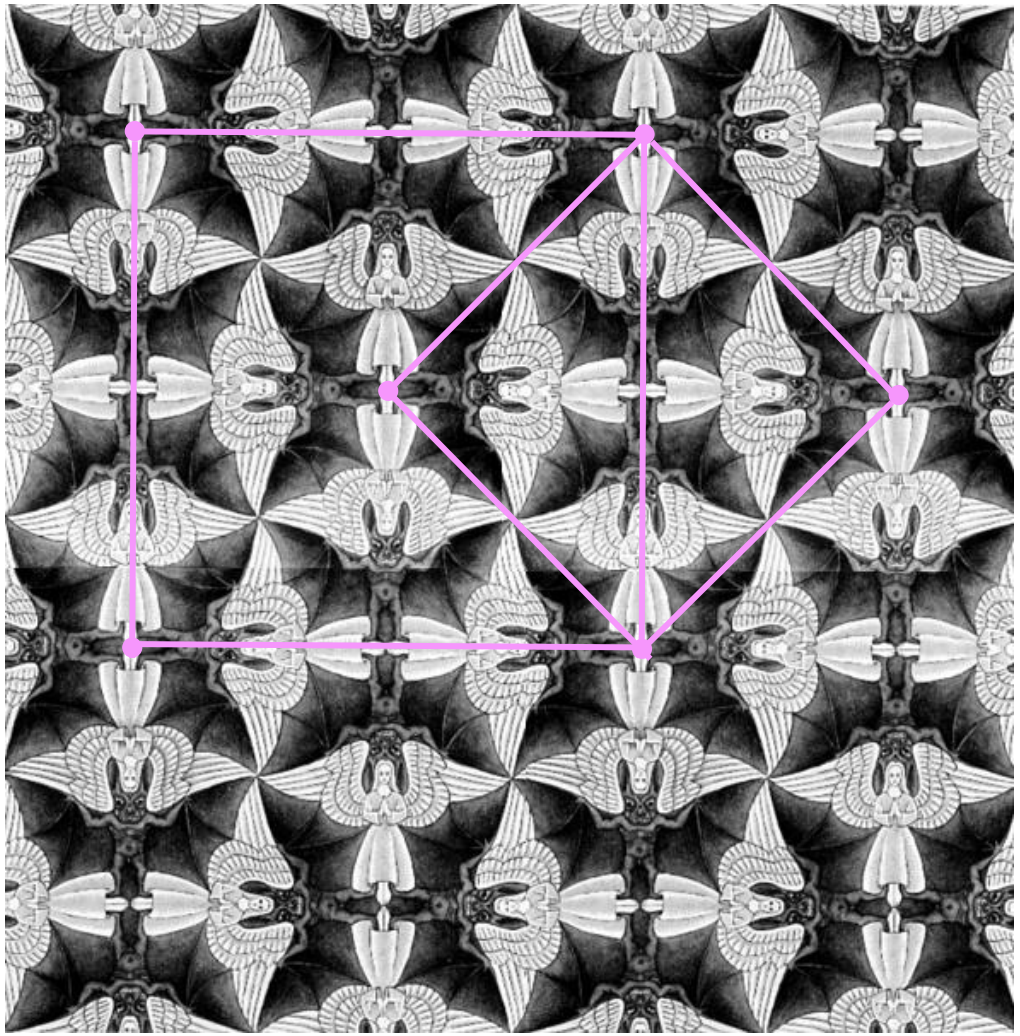
MONOCLINIC
$a \neq b \neq c$
$\alpha = \gamma = 90°$
$\beta \neq 120°$



TRICLINIC
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$



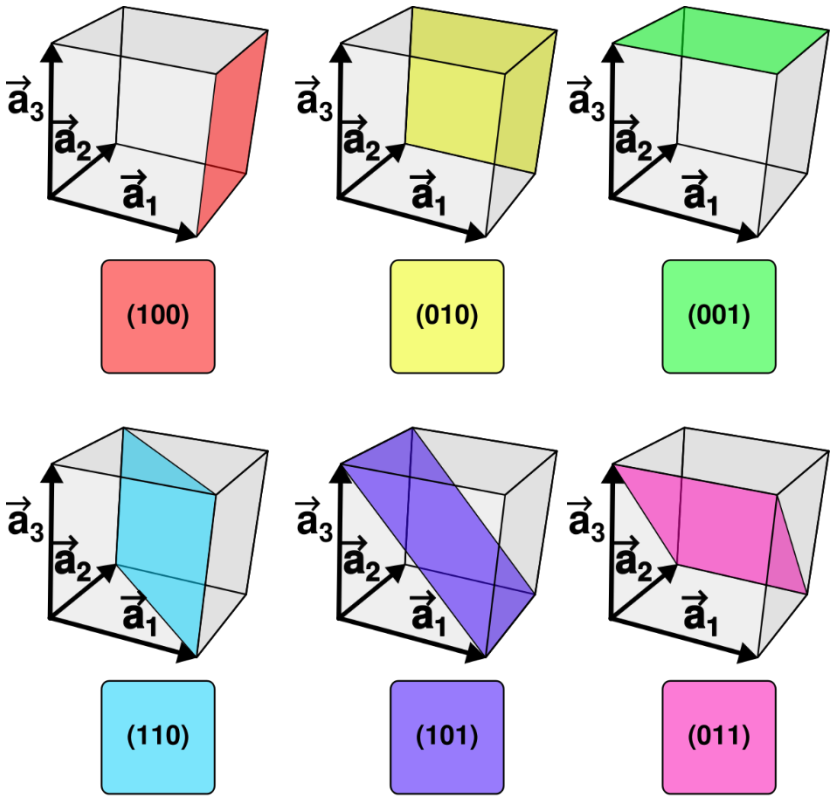
http://www.chm.bris.ac.uk/webprojects2003/cook/latticetypes.htm



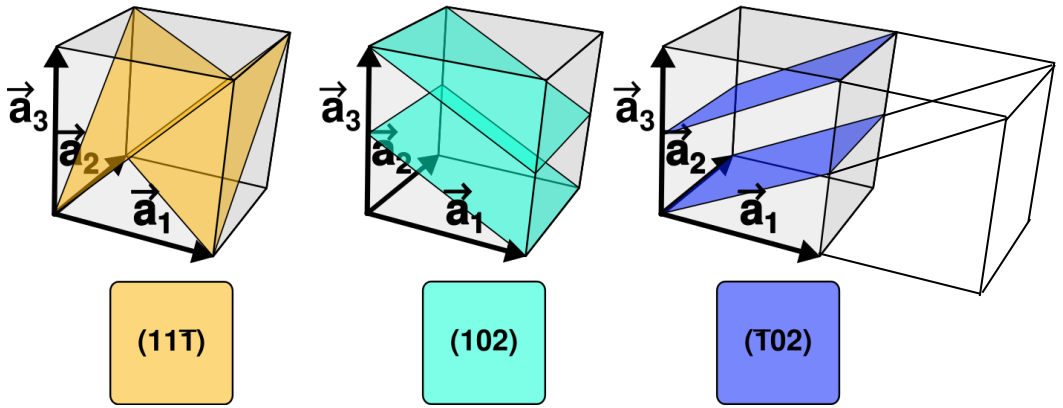
Systematic absences for extra symmetry

Miller indeces (h k l)

$n\lambda = 2\mathbf{d}\sin(\theta)$ Bragg's law



- What are the dots that scatter elastically the X-rays in crystals?



Indexing

$n\lambda = 2\mathbf{d}\sin(\theta)$ Bragg's law

Cubic
$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Tetragonal
$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Orthorhombic
$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Hexagonal
$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

Monoclinic
$$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

Triclinic
$$\frac{1}{d^2} = \frac{1}{V^2}[h^2b^2c^2\sin^2\alpha + k^2a^2c^2\sin^2\beta + l^2a^2b^2\sin^2\gamma + 2hkabc^2(\cos\alpha\cos\beta - \cos\gamma) + 2kla^2bc(\cos\beta\cos\gamma - \cos\alpha) + 2hlab^2c(\cos\alpha\cos\gamma - \cos\beta)]$$

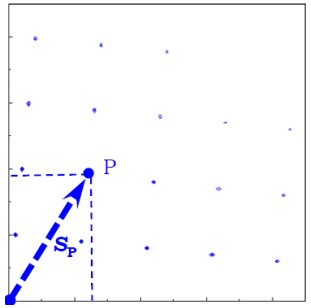
Systematic absences for extra symmetry

Structure factor

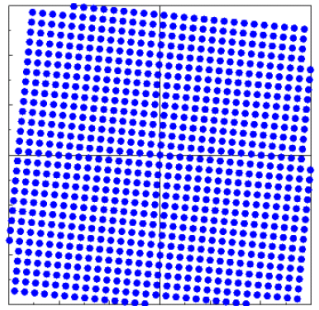
$$I_{hkl} \propto |F_{hkl}|^2$$

$$F_{hk\ell} = \sum_{j=1}^{N} f_j \mathrm{e}^{[-2\pi i(hx_j + ky_j + \ell z_j)]}$$

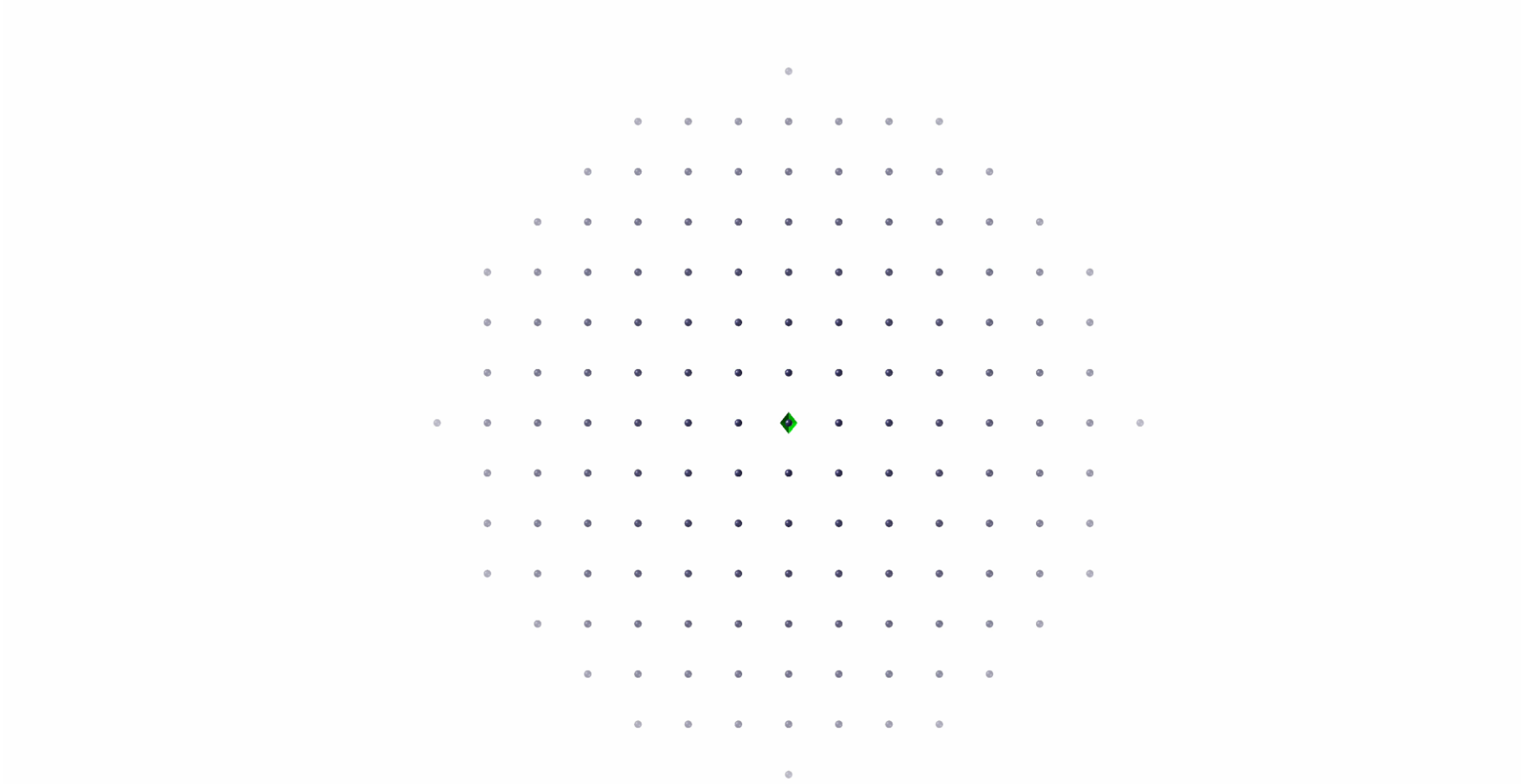
Powder Diffraction



Single

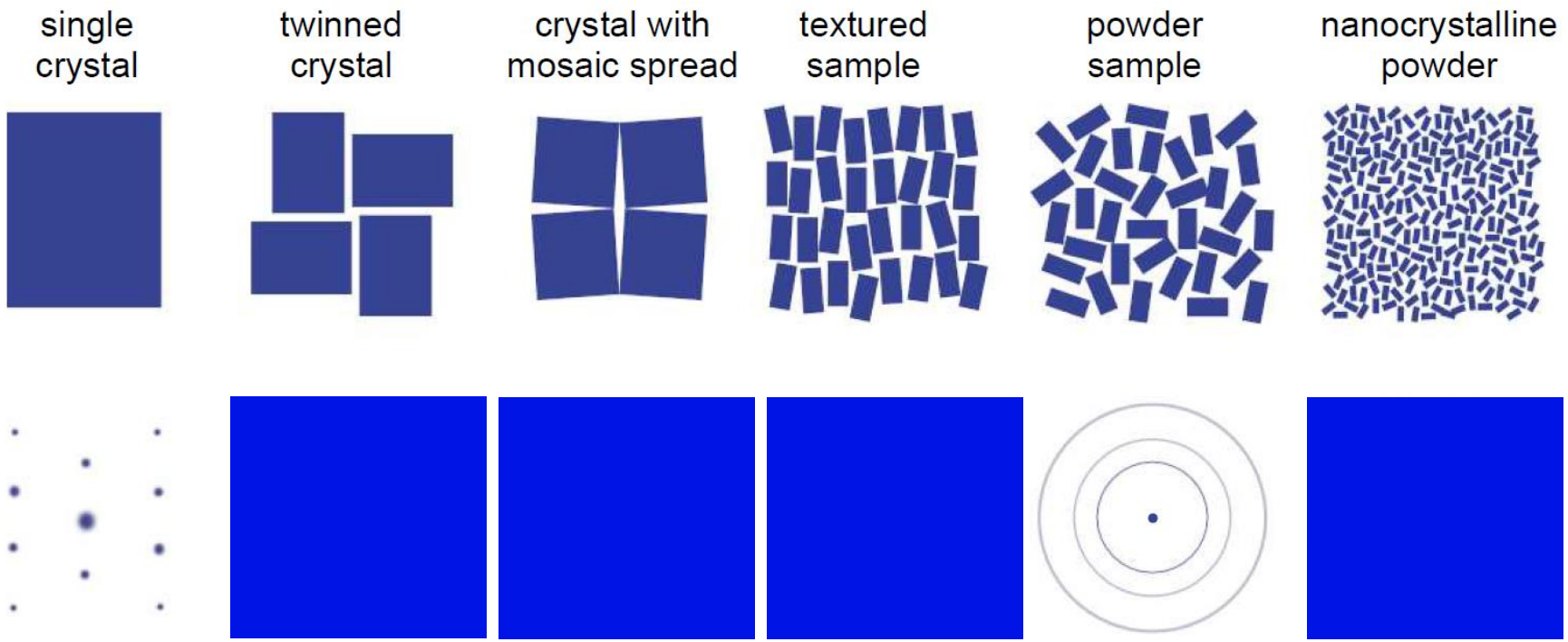


After S. Galli, SLS - Powder Diffraction School 2016

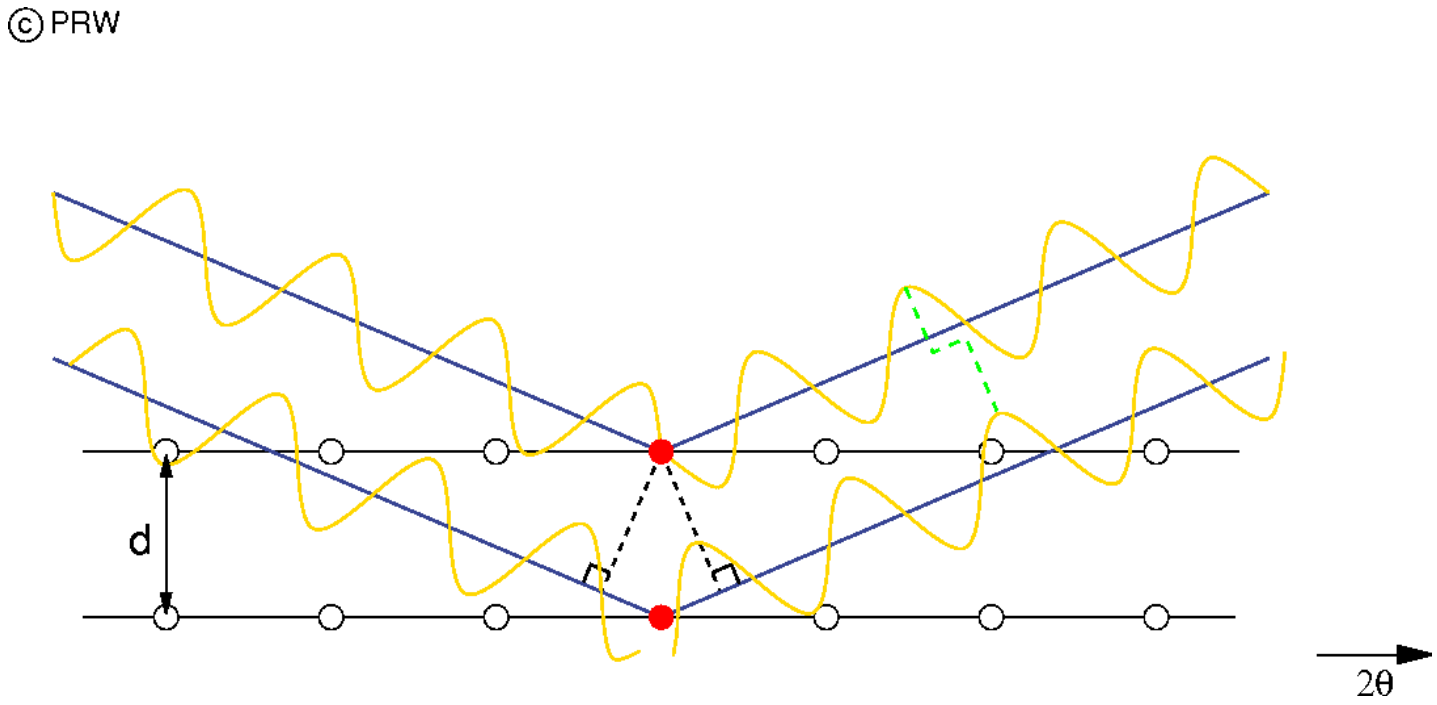


www.synchrotronmovies.com

Different objects for diffraction



That equation ...



$$m\lambda = 2d \sin \theta$$

Diffractogram

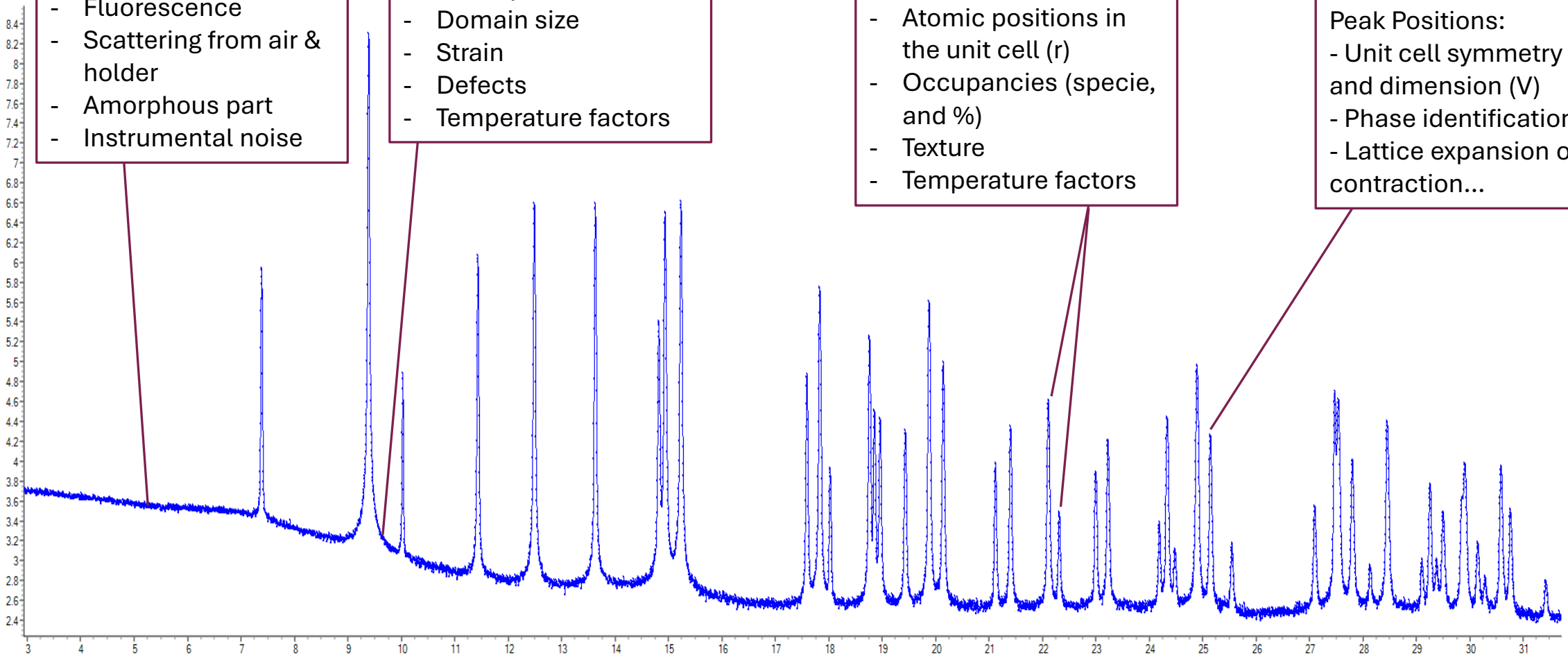
PSI

Background
- Diffuse scattering
- Fluorescence
- Scattering from air & holder
- Amorphous part
- Instrumental noise

Peak Shape
- Domain size
- Strain
- Defects
- Temperature factors

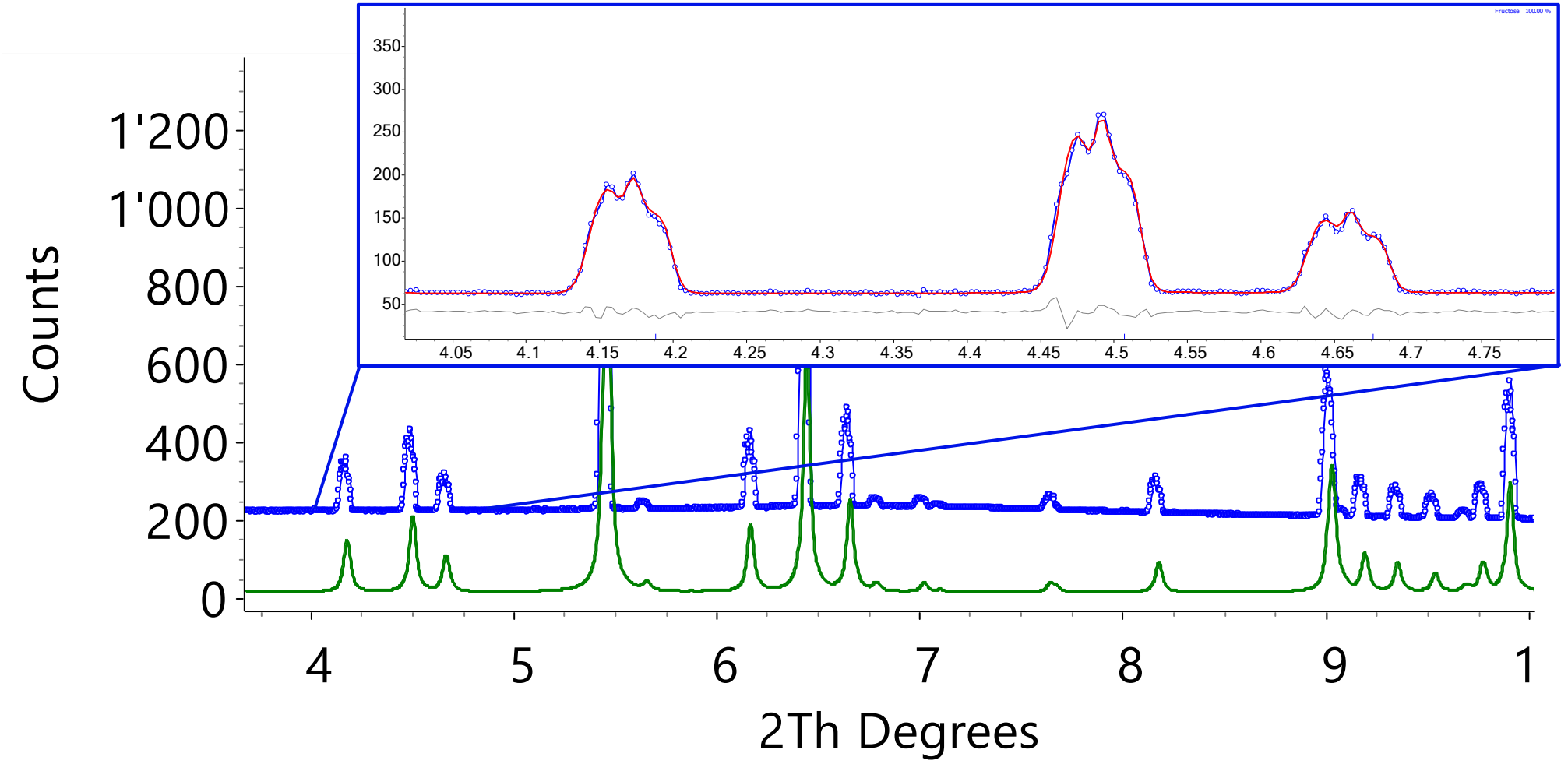
Peak Intensities
- Atomic positions in the unit cell (r)
- Occupancies (specie, and %)
- Texture
- Temperature factors

Peak Positions:
- Unit cell symmetry and dimension (V)
- Phase identification
- Lattice expansion or contraction...



Peak broadening

- Instrument
- Setup
- Sample



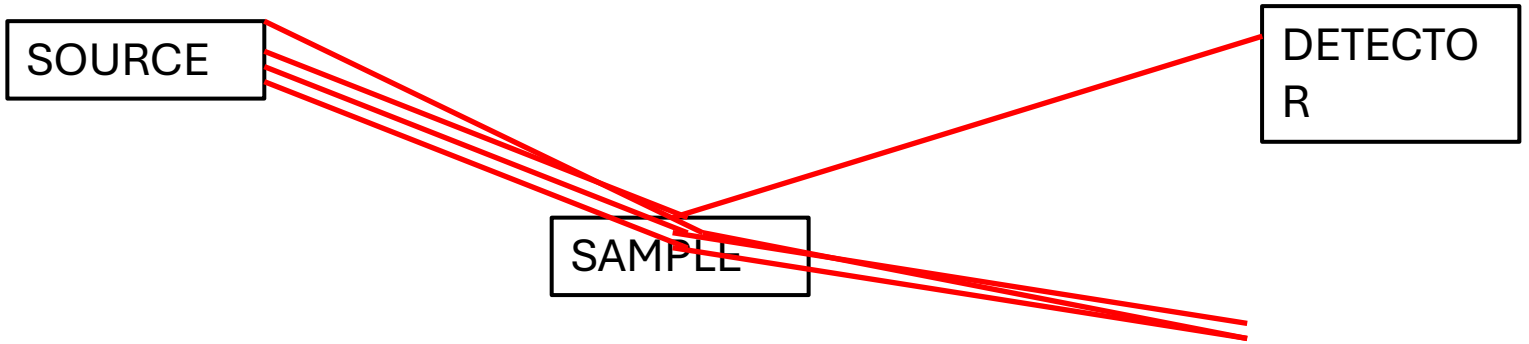
Sample, Instrument, Measurement, Data

- Everything contributes to your data
- No measurement is ever ‘perfect’
- Info you are looking for are mixed with info you do not need (or you should already know …)
- Wrong start, wrong end!

The better you can see

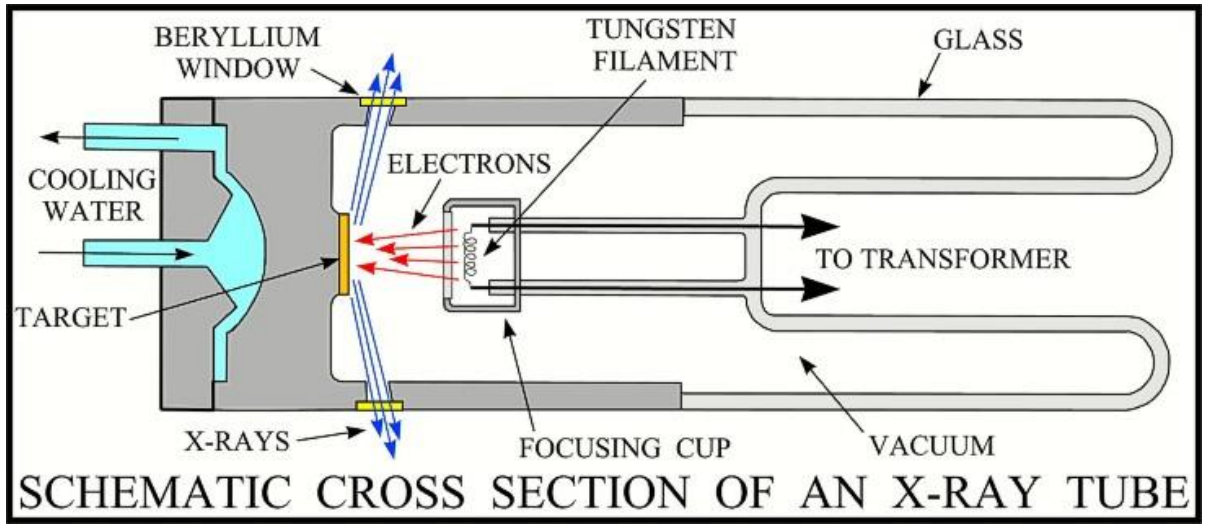
the more the details become relevant

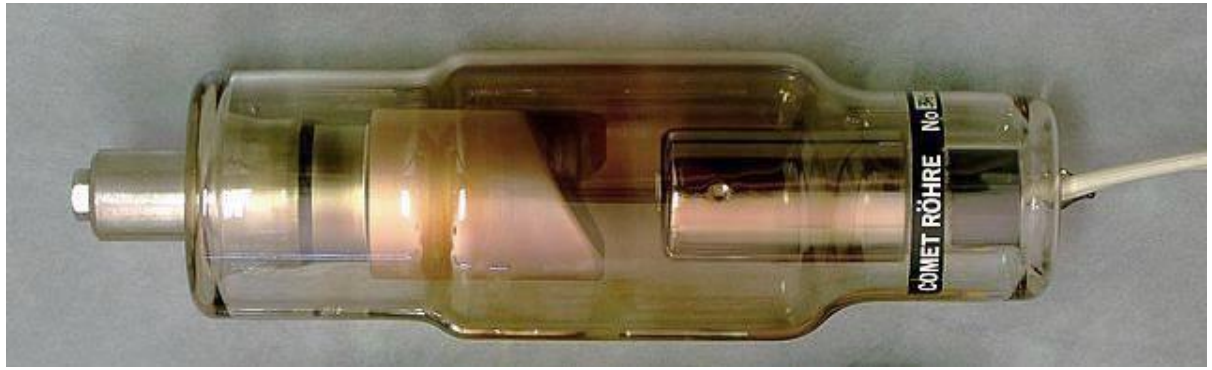
Diffraction measurement/experiment



Optical elements can be used in combination to produce various setups, with different characteristics

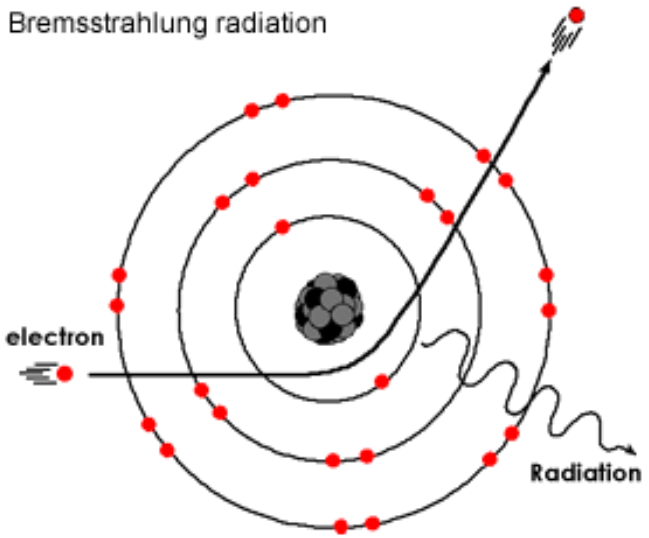
Source – X-ray tube

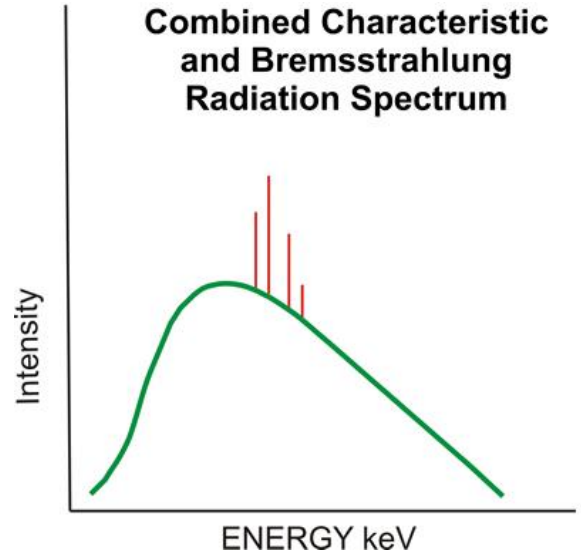


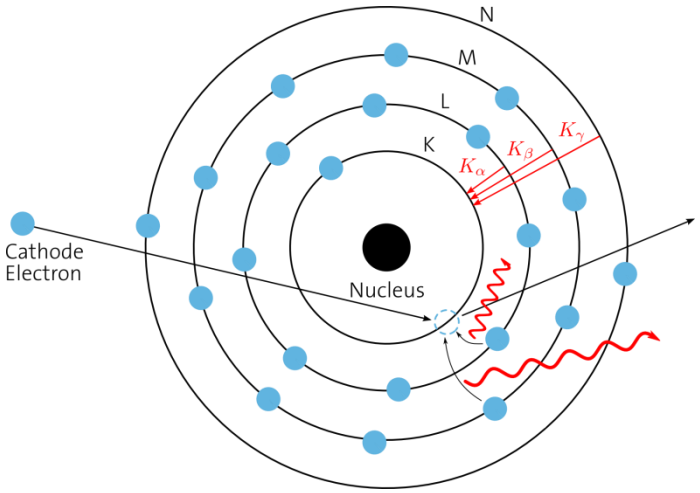


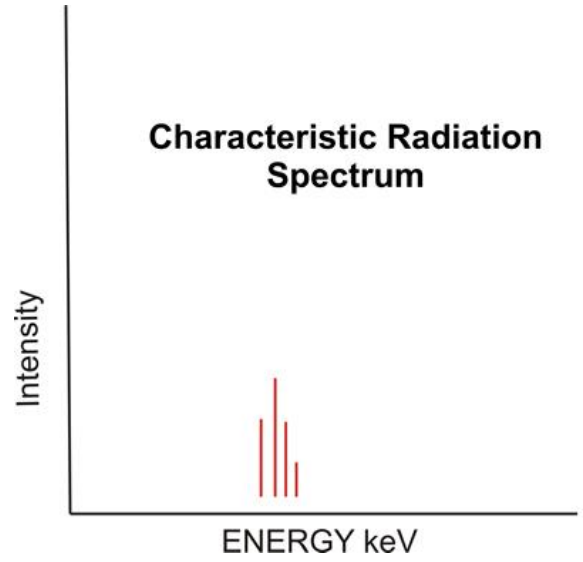
- Standard Targets: Cu/Mo/Ag

Source – X-ray tube

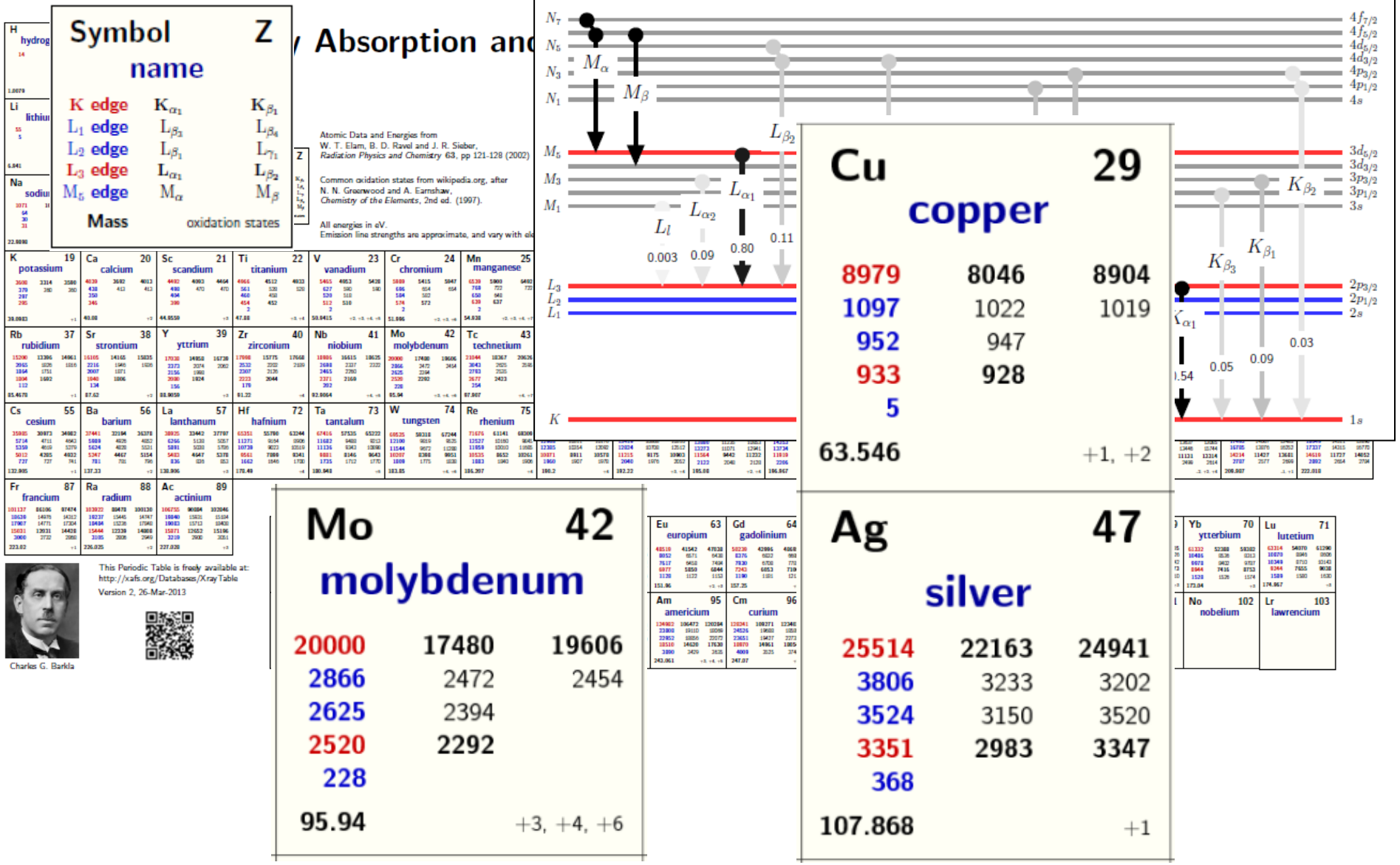








Binding Energies



Source – X-ray tube

λ = 12.39842 / E(keV)

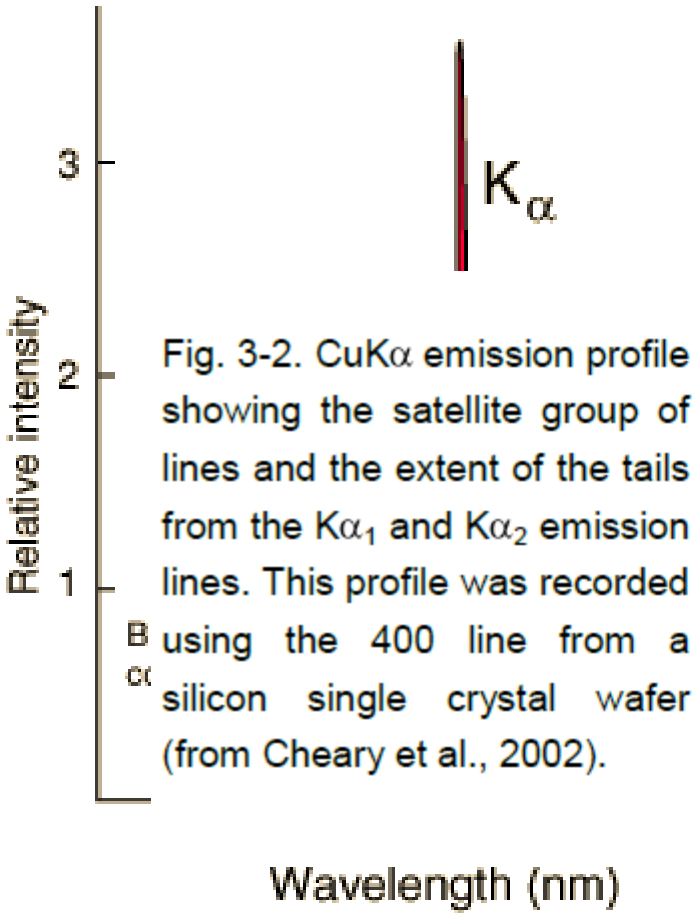
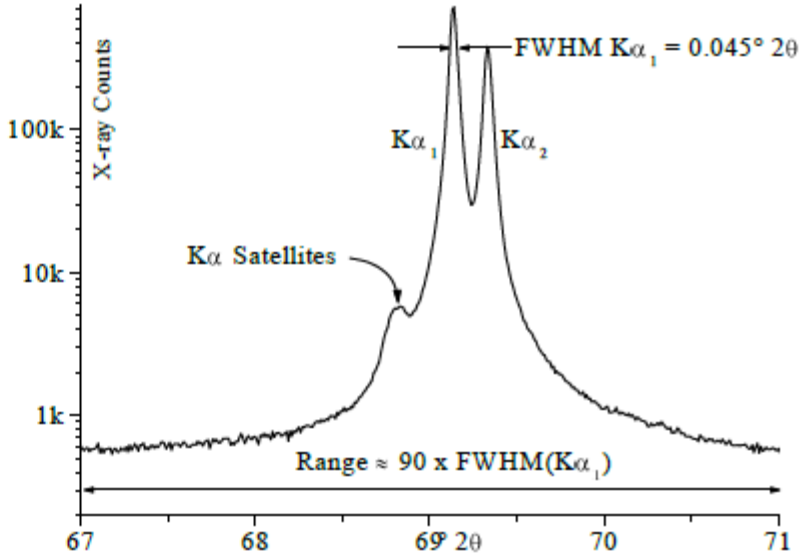
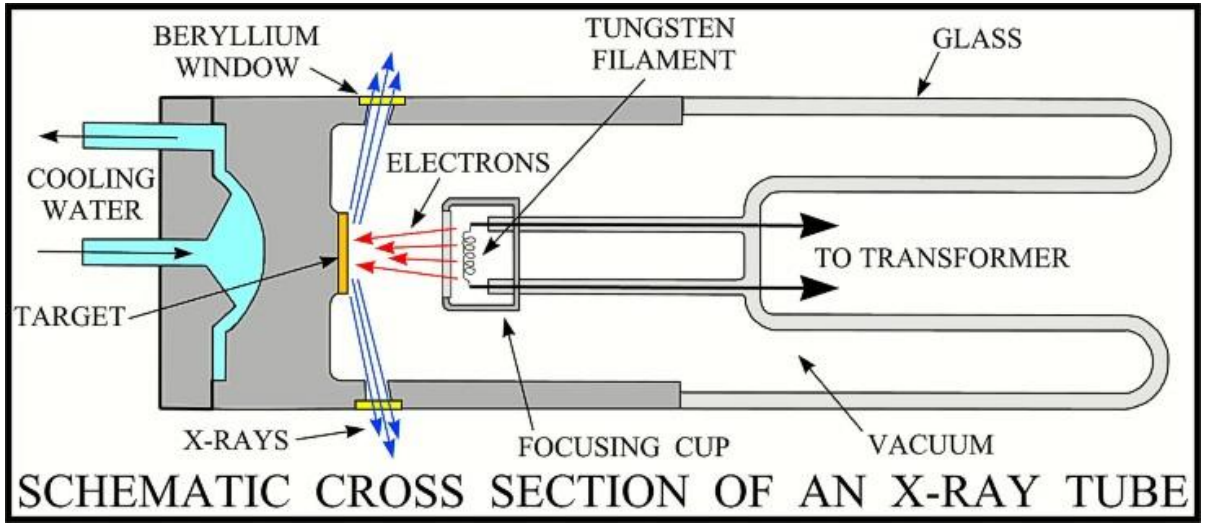


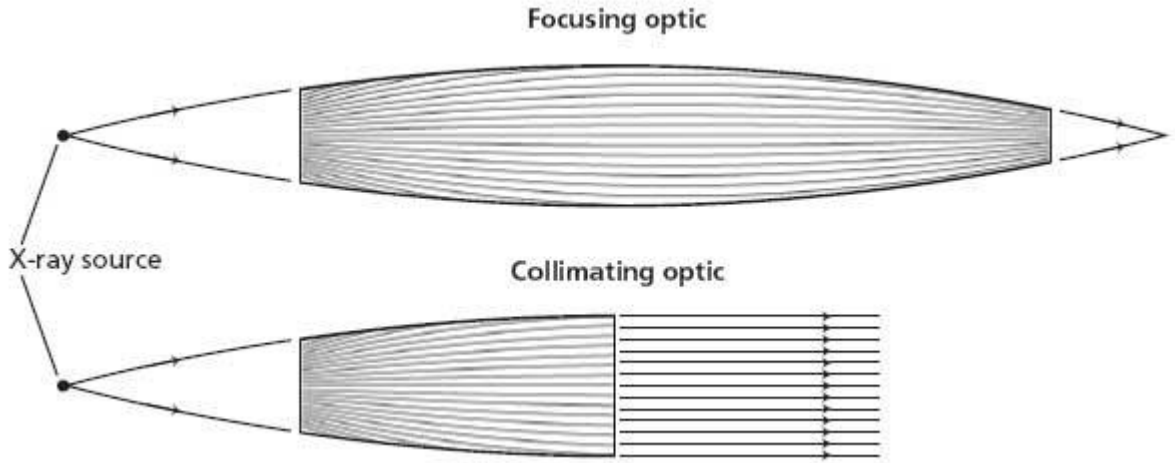
Fig. 3-2. CuKα emission profile showing the satellite group of lines and the extent of the tails from the $K\alpha_1$ and $K\alpha_2$ emission lines. This profile was recorded using the 400 line from a silicon single crystal wafer (from Cheary et al., 2002).



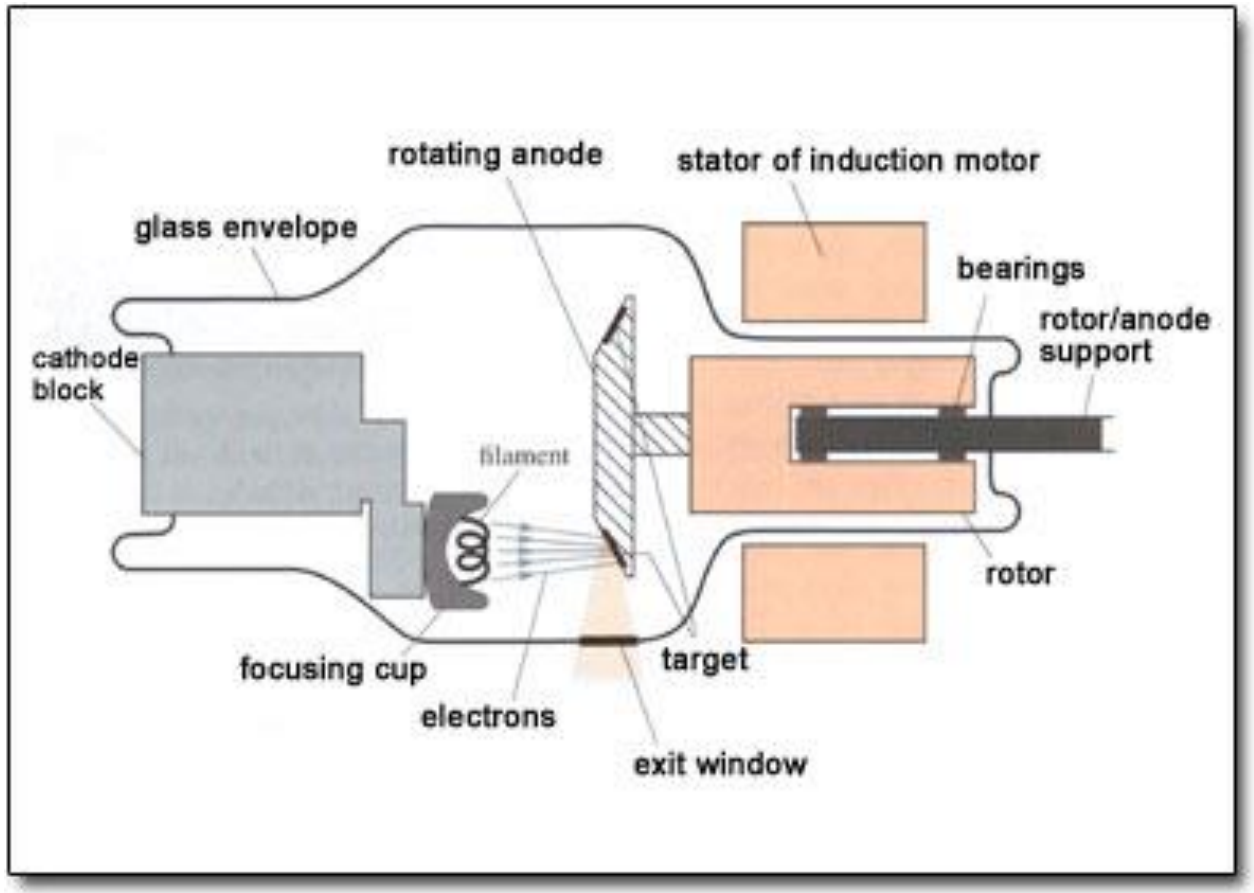
Source – X-ray tube



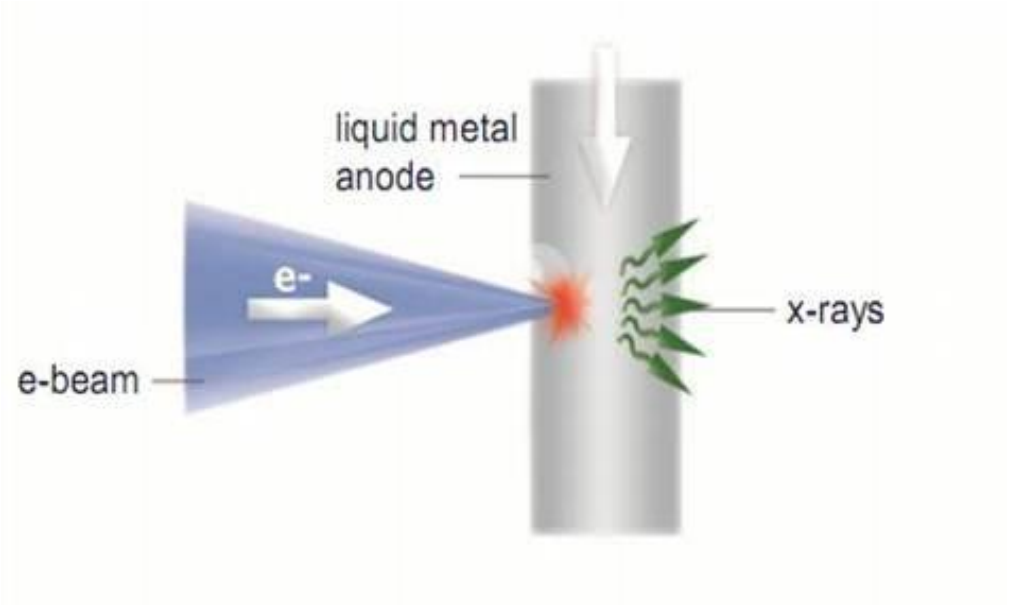
- Several kV and mA, several kW/mm^2

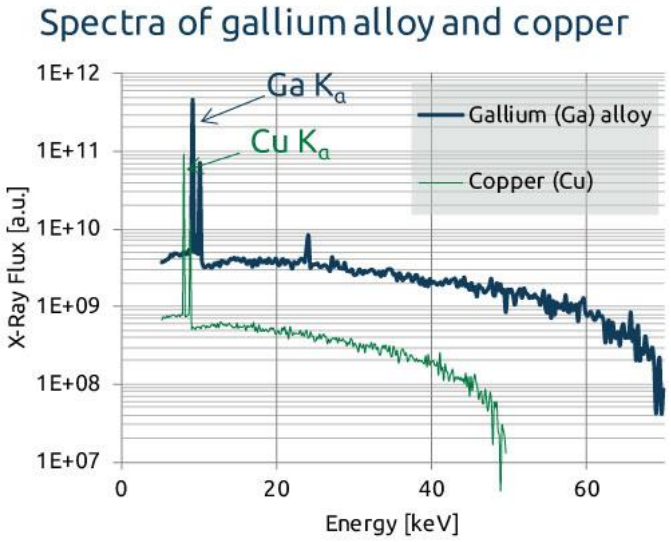


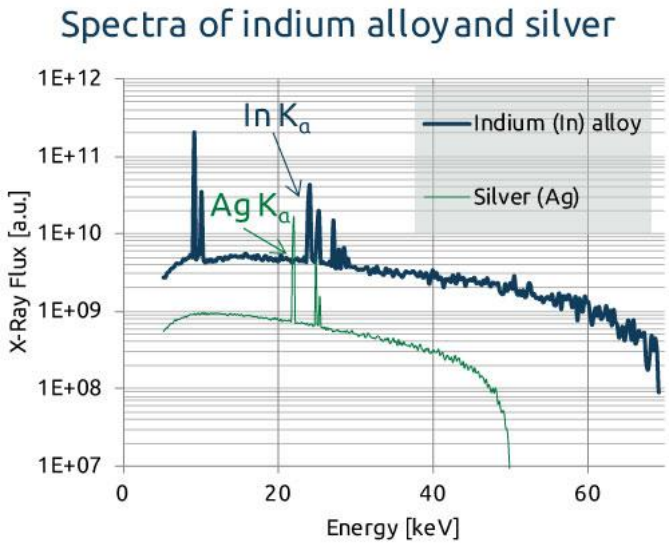
Rotating anode



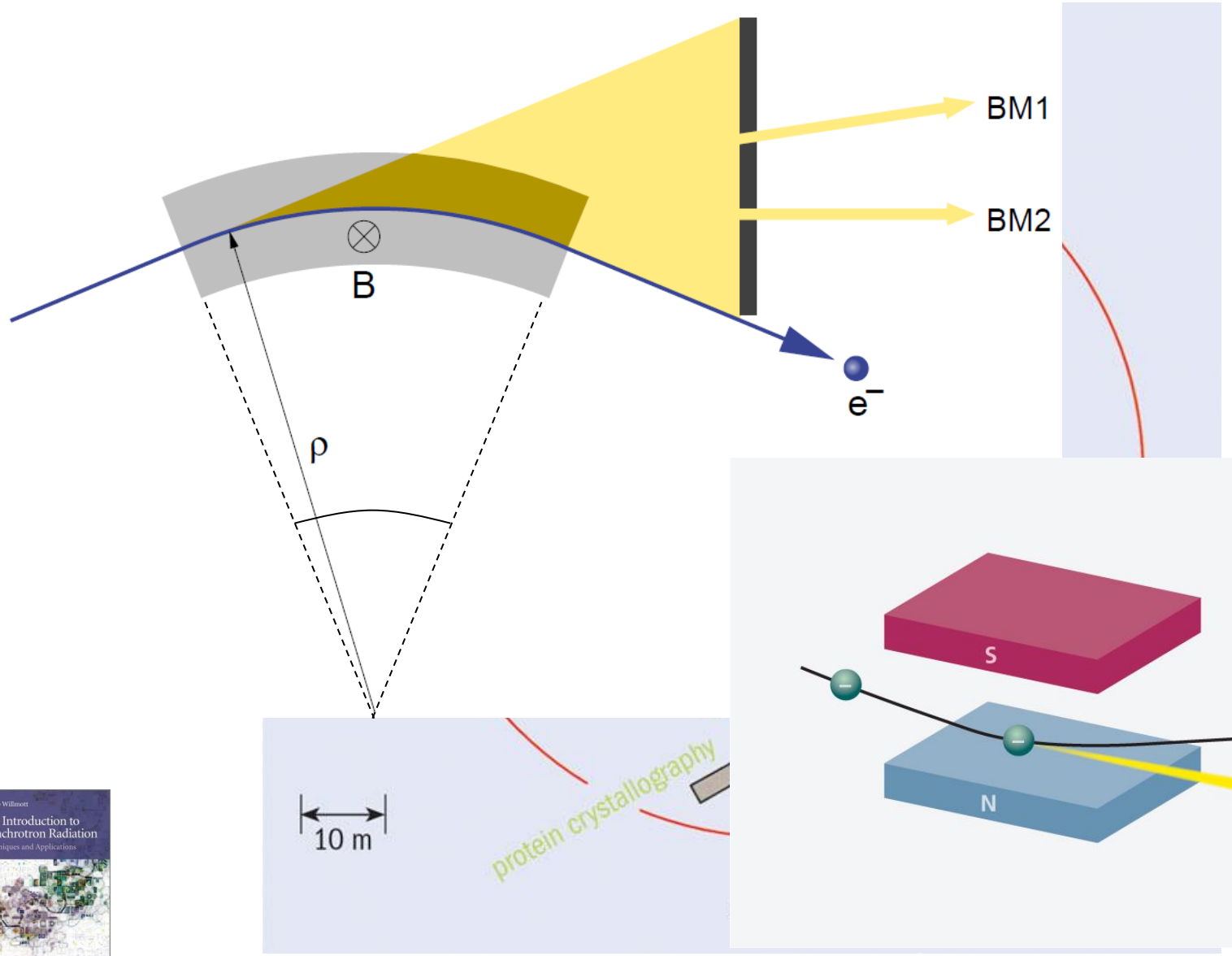
Liquid jet


liquid metal
anode
e-
e-beam
x-rays


Spectra of gallium alloy and copper
Ga Kα
Cu Kα
Gallium (Ga) alloy
Copper (Cu)
X-Ray Flux [a.u.]
1E+12
1E+11
1E+10
1E+09
1E+08
1E+07
0
20
40
60
Energy [keV]


Spectra of indium alloy and silver
In Kα
Ag Kα
Indium (In) alloy
Silver (Ag)
X-Ray Flux [a.u.]
1E+12
1E+11
1E+10
1E+09
1E+08
1E+07
0
20
40
60
Energy [keV]

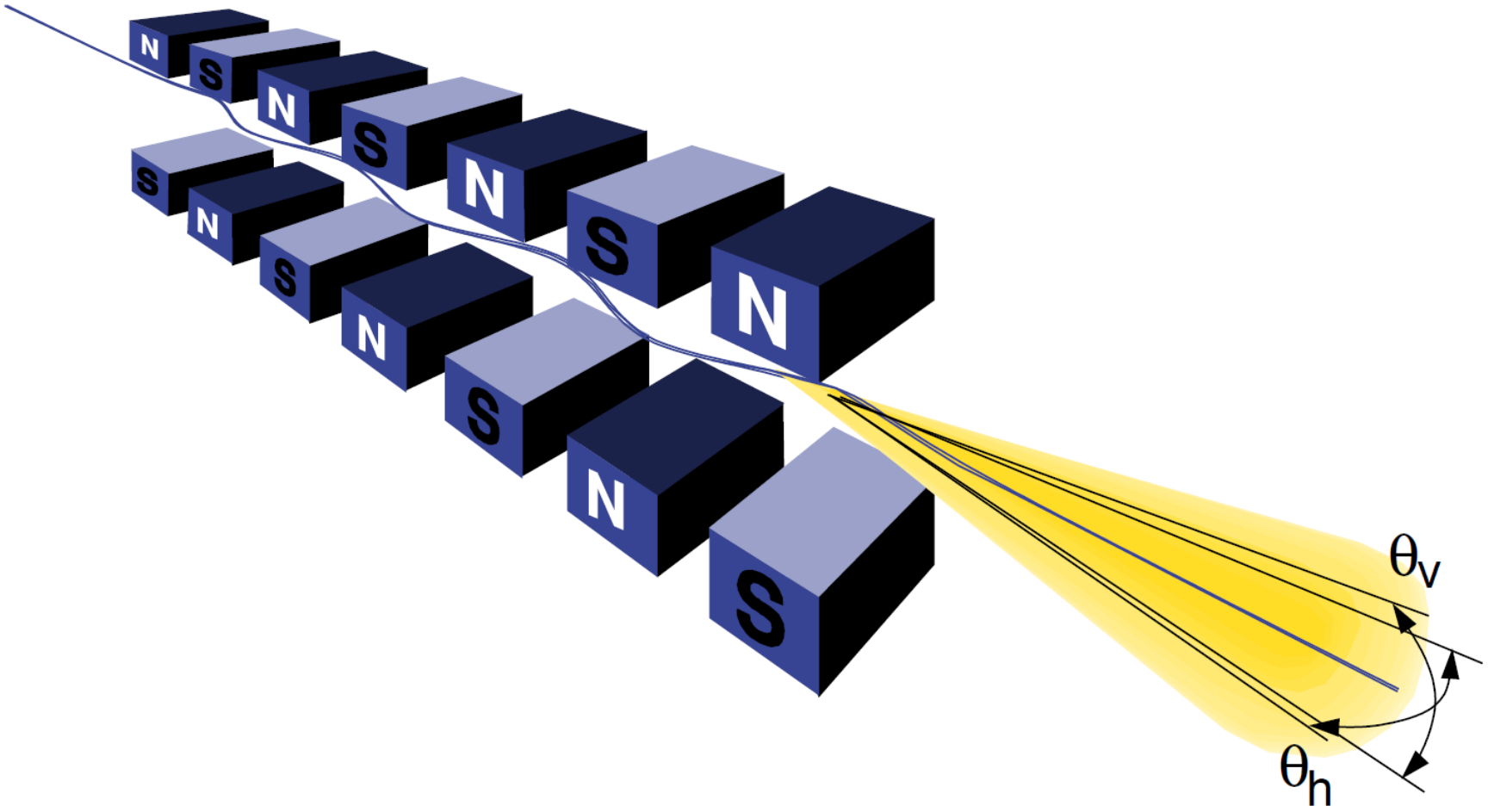
Synchrotron – bending the electrons



TOP UP MODE

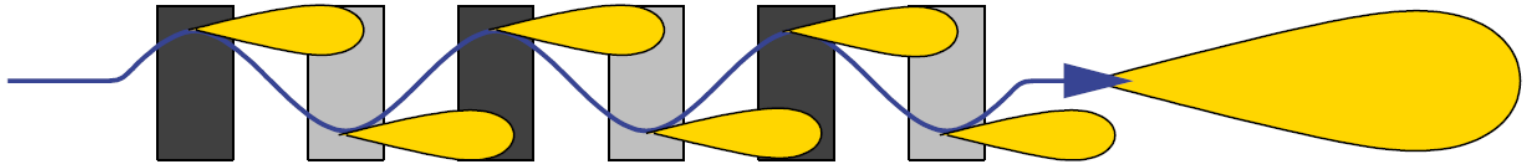
Insertion devices

PSI

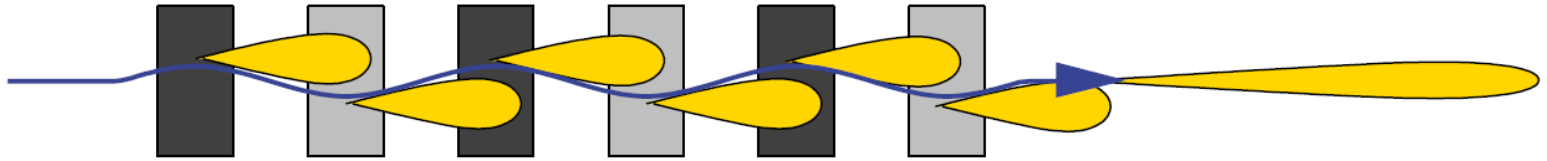


Insertion devices

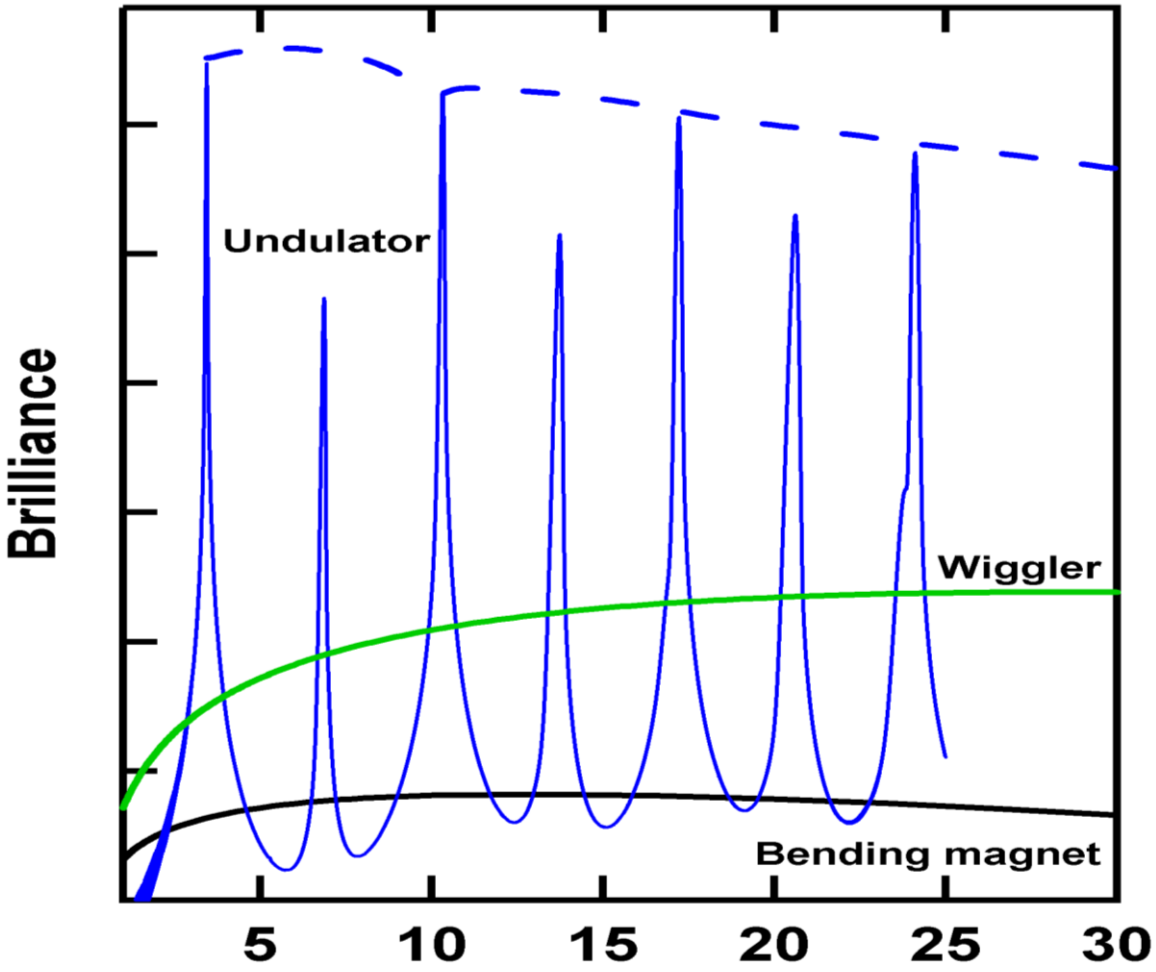
(a) Wiggler



(b) Undulator

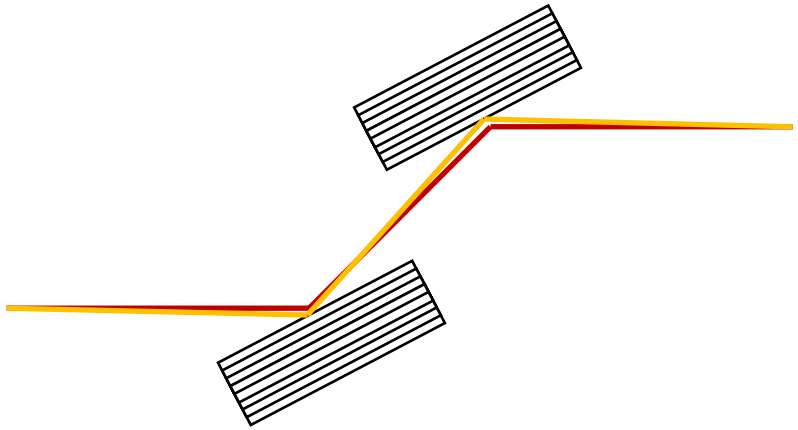


Insertion devices



λ = 12.39842 / E(keV)

Monochromator

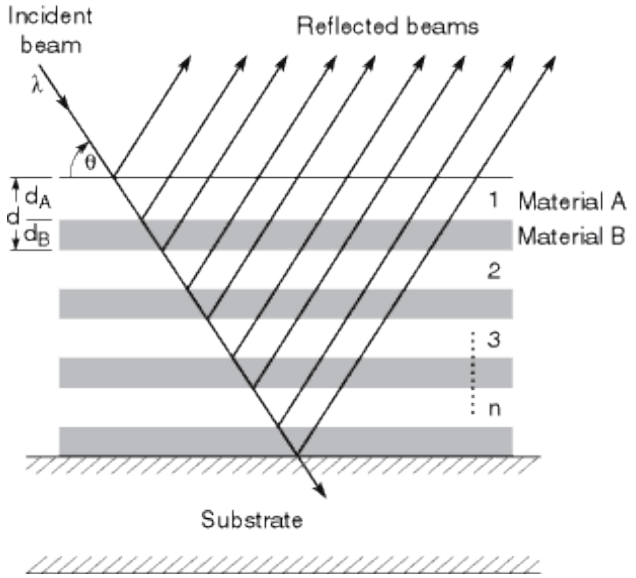


Crystal

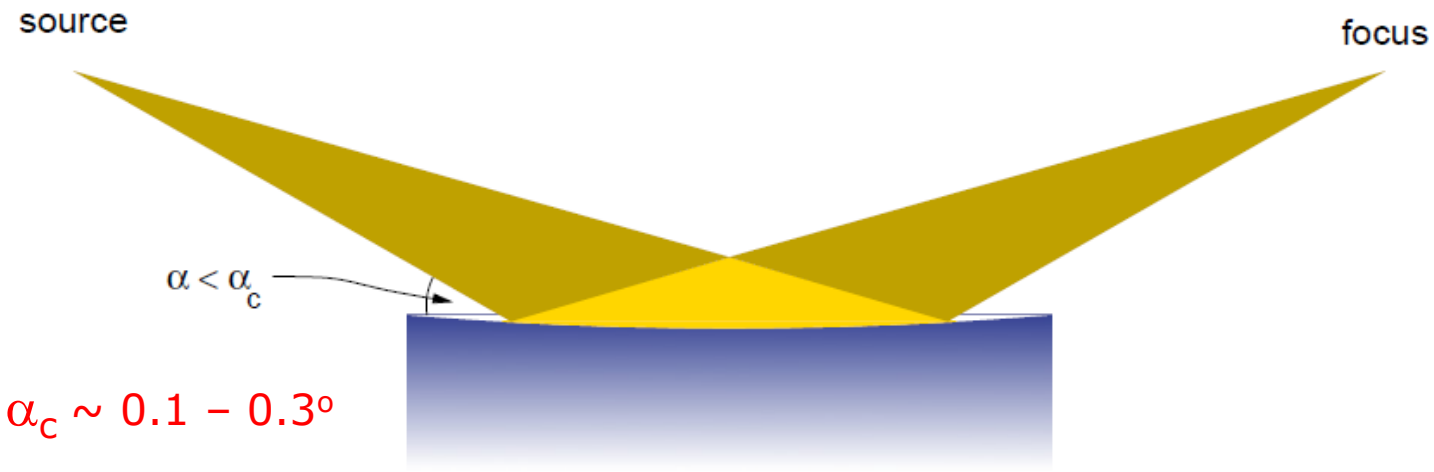
- λ < ~ 1 nm

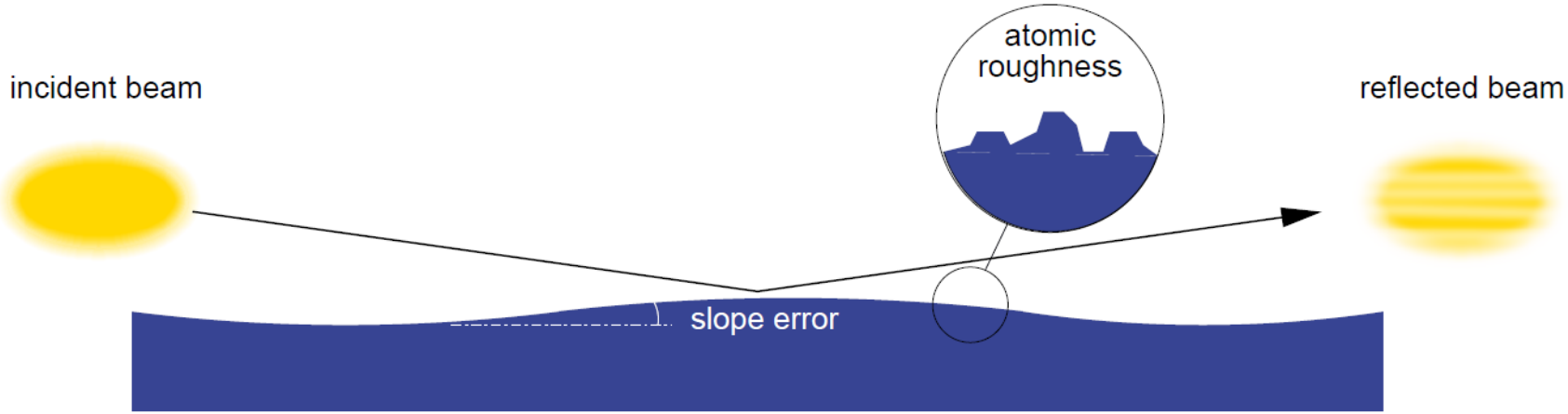
Multilayer

- $\Delta\lambda/\lambda$ larger (more Flux!)

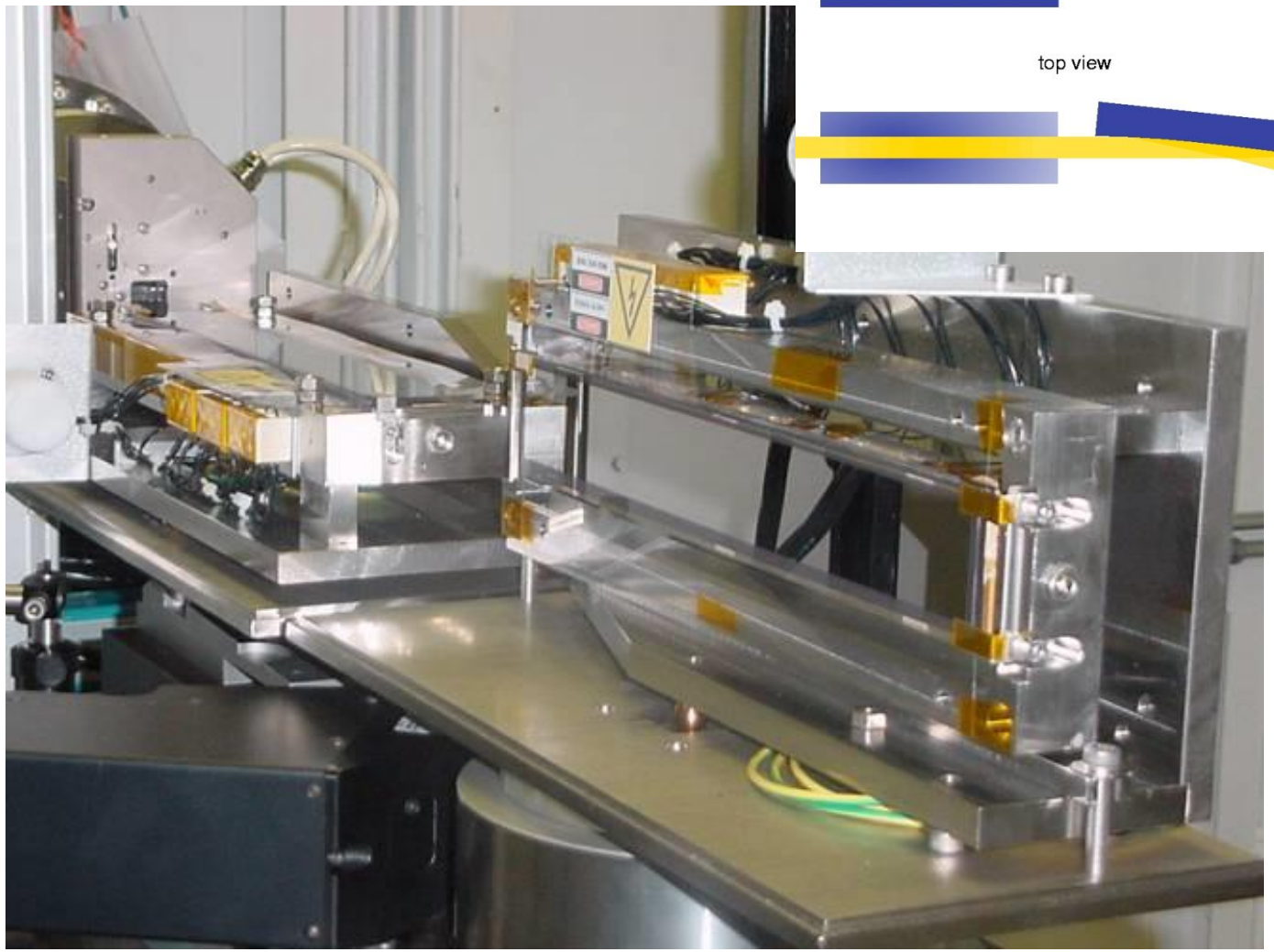


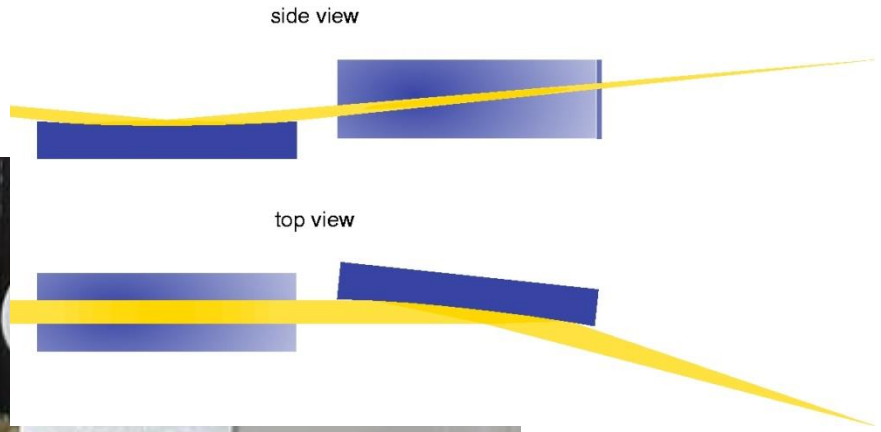
Mirrors


source
focus
$\alpha < \alpha_c$
$\alpha_c \sim 0.1 - 0.3^o$

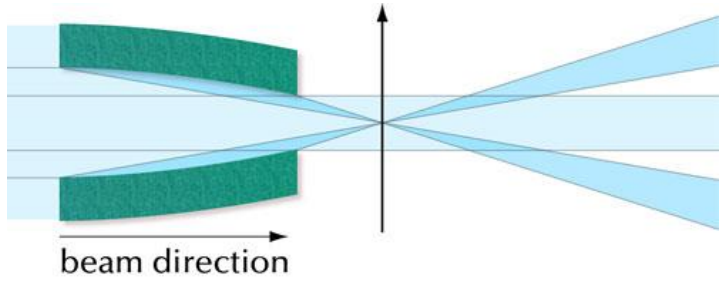

incident beam
atomic roughness
reflected beam
slope error

Focussing mirrors

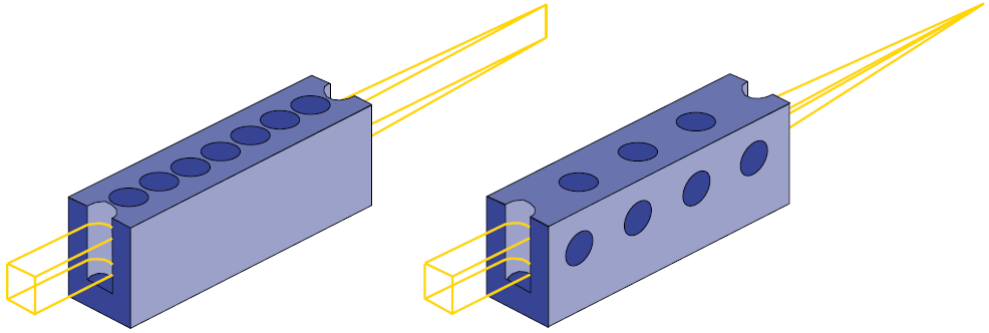




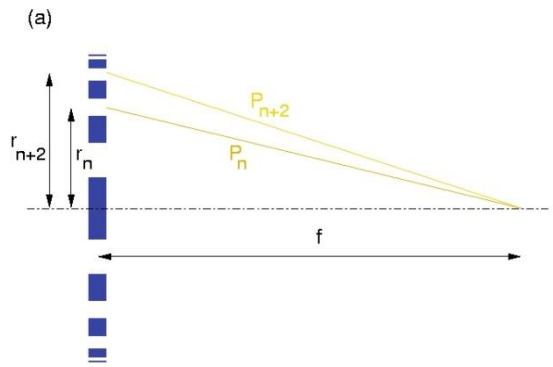
Focussing

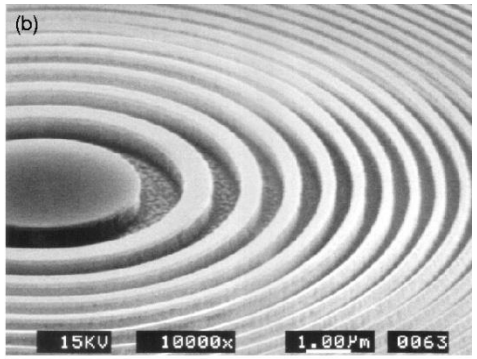


- Glass capillaries

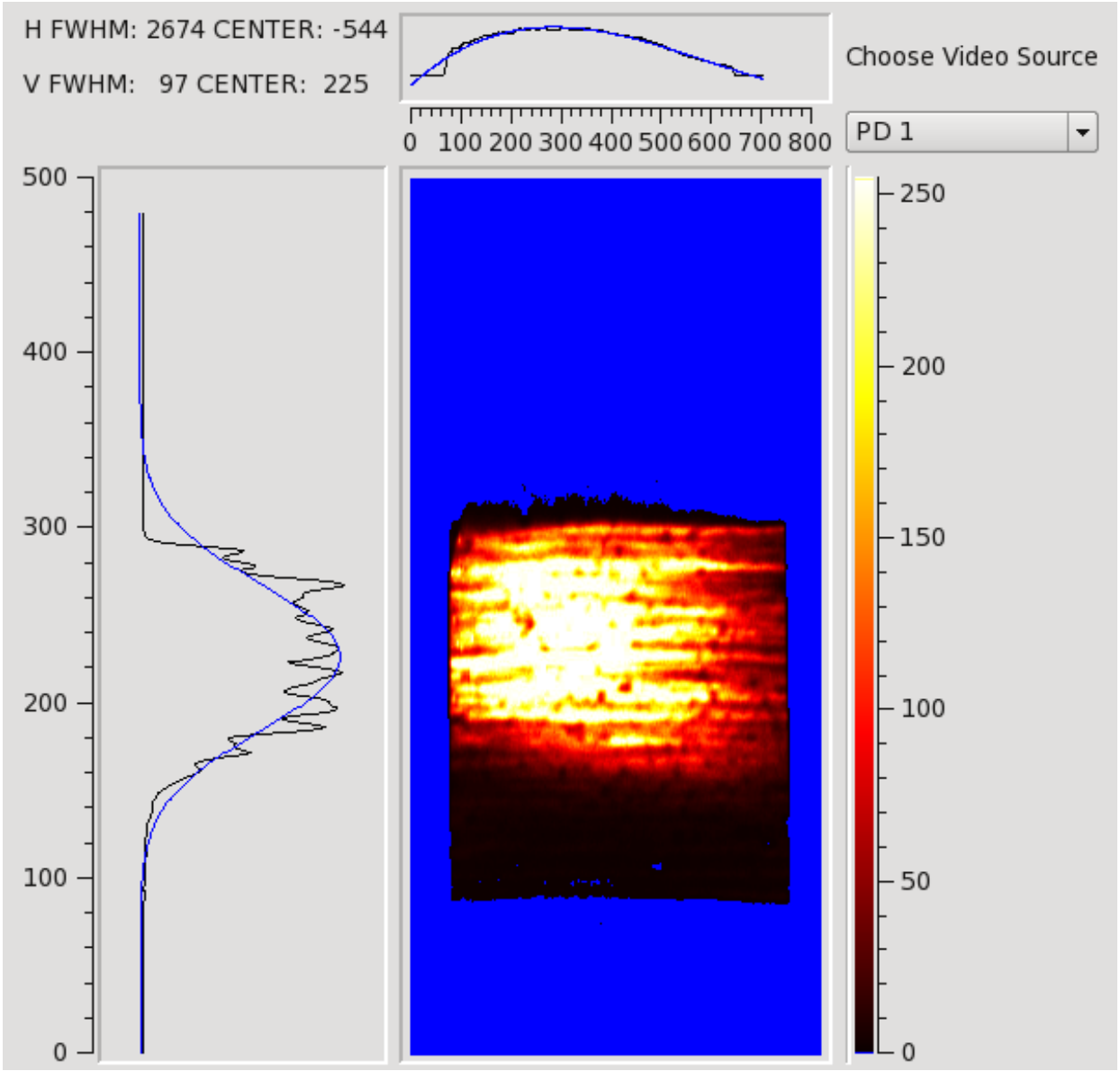


- Compound refractive lenses
- Fresnel Zone plates



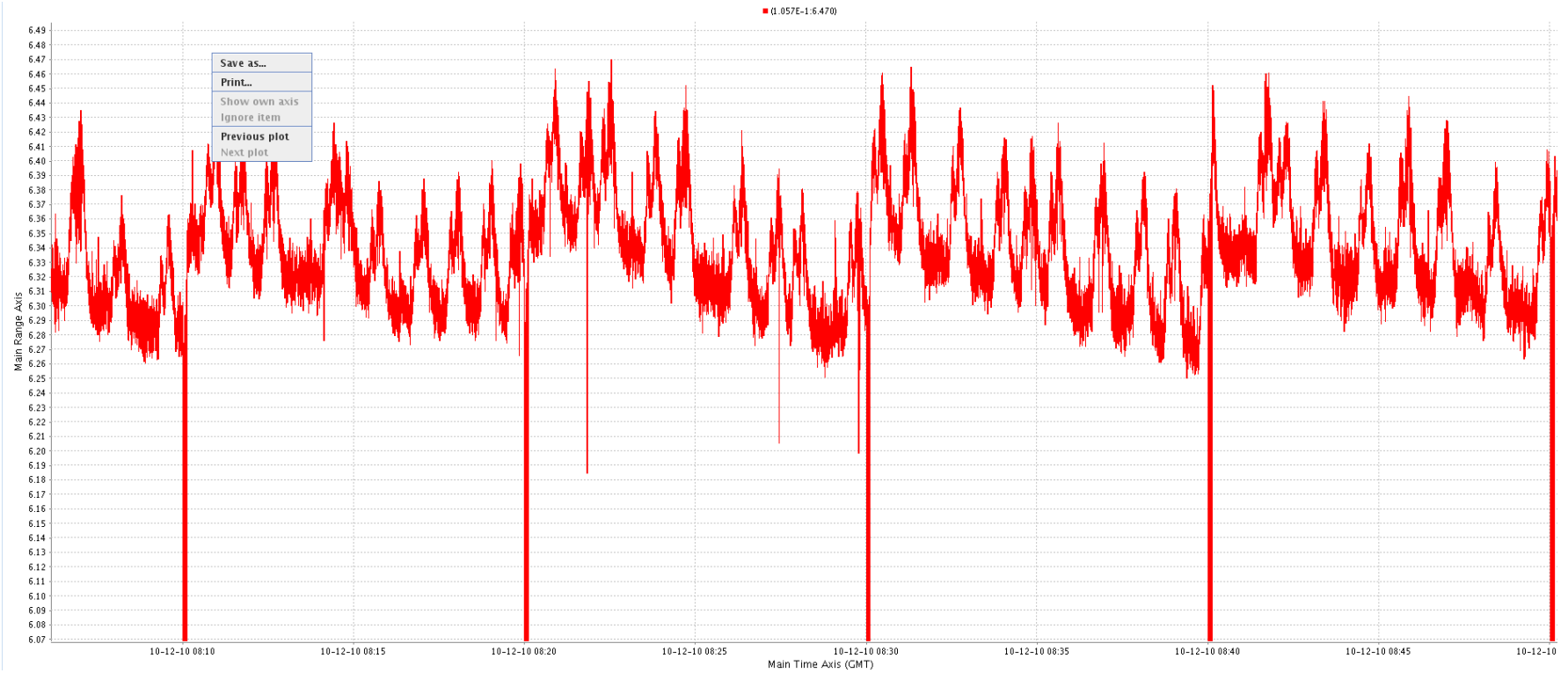


Optical elements



- Wavelengths
- Focusing
- Insertion device
- Mirrors

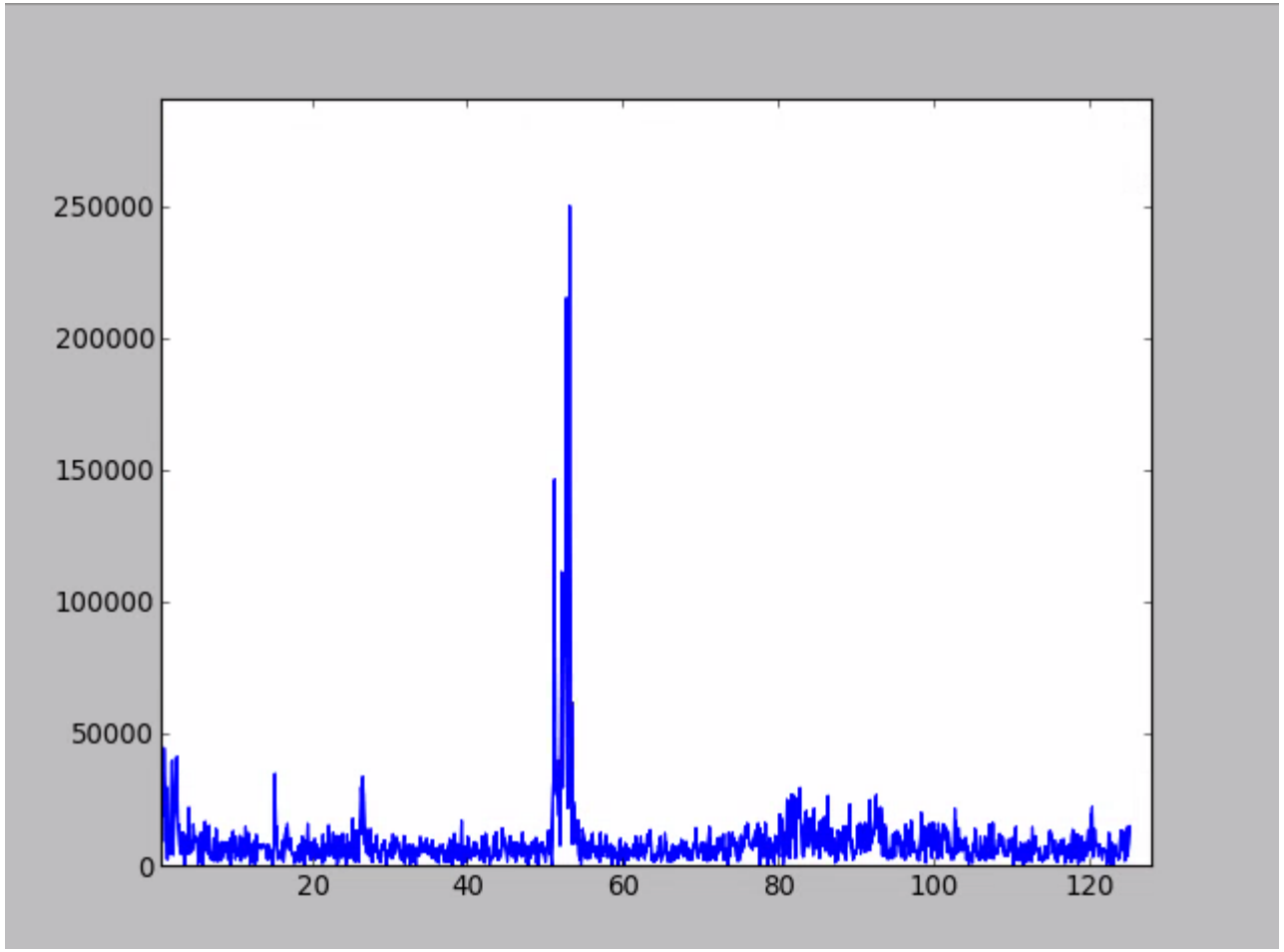
Intensity fluctuation



Intensity monitor

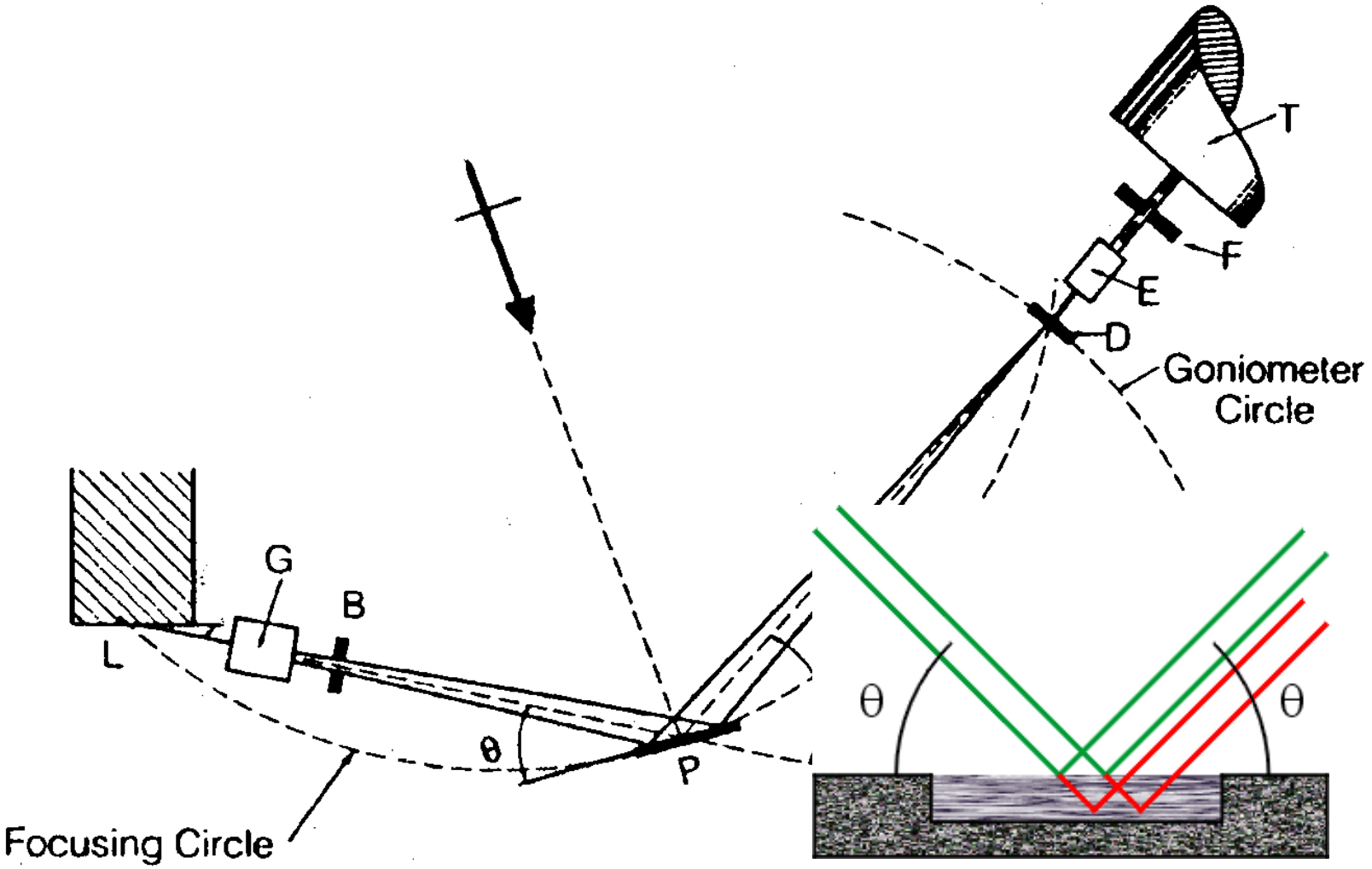
Don’t collect at topups

Beam vibration

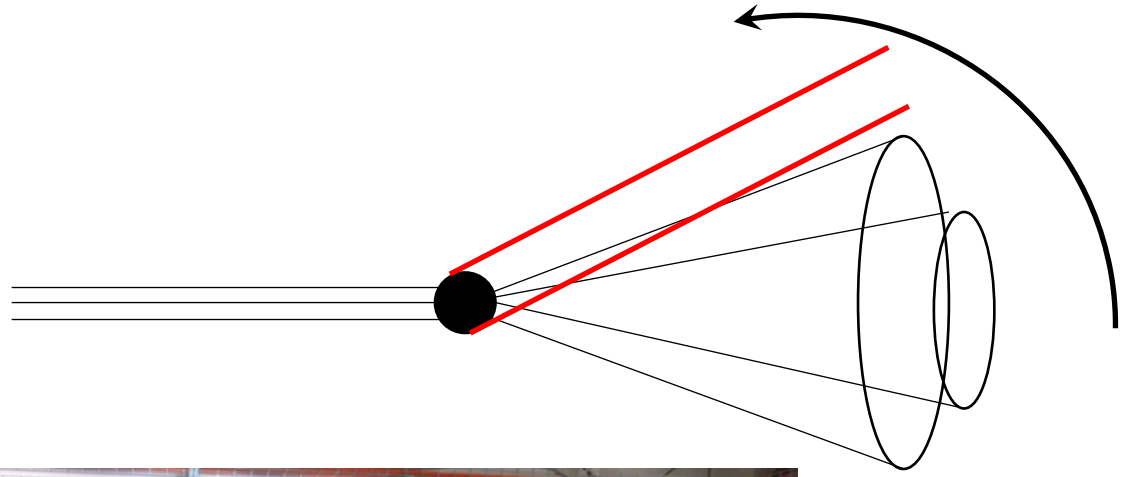


Check your position!

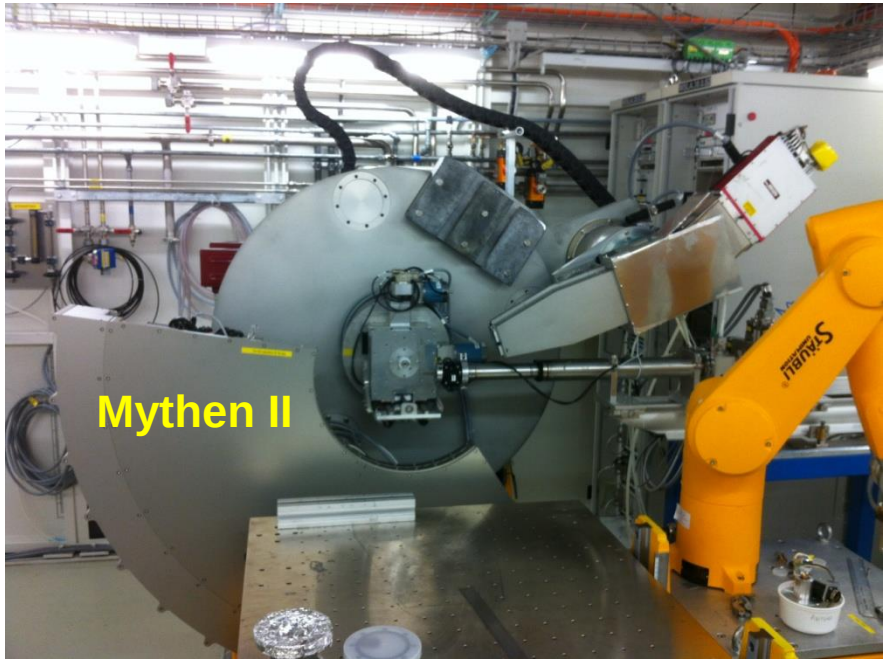
Bragg-Brentano



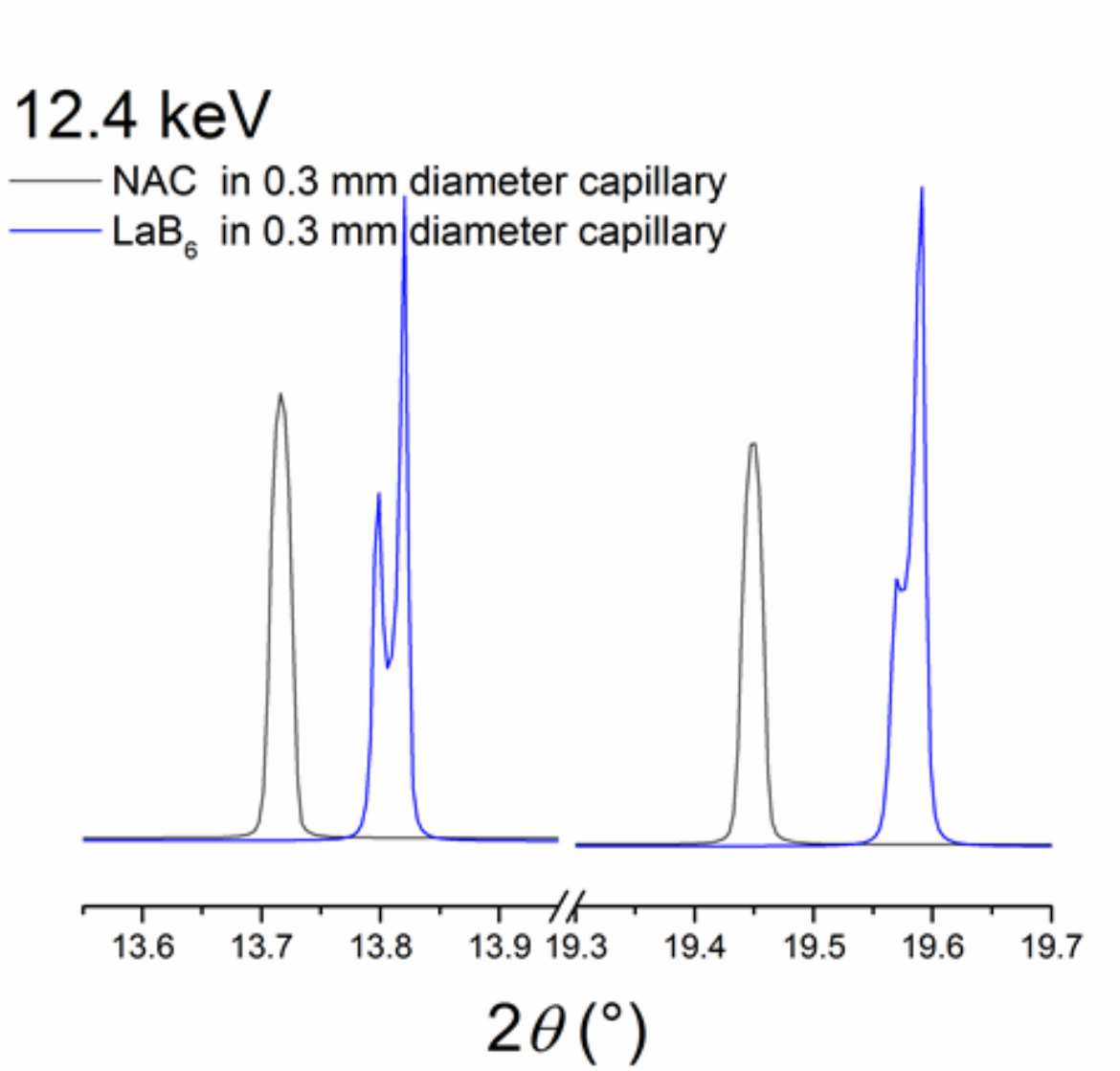
Debye-Scherrer



- Smaller sample, easy spinning
- Size matters



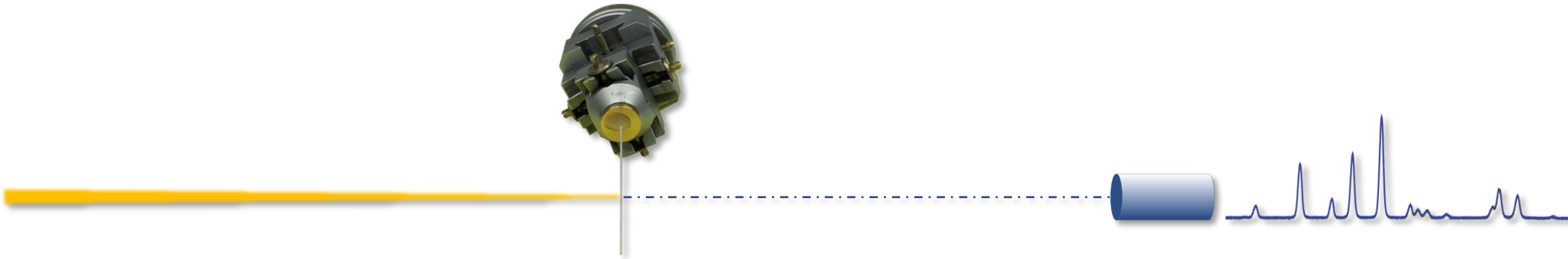
Absorption


12.4 keV
NAC in 0.3 mm diameter capillary
LaB6 in 0.3 mm diameter capillary
13.6
13.7
13.8
13.9
19.3
19.4
19.5
19.6
19.7
2θ(°)

PXRD and detectors

Acquisition time
~ hours

Ye olde method…



More detectors ...

Multiple single detectors

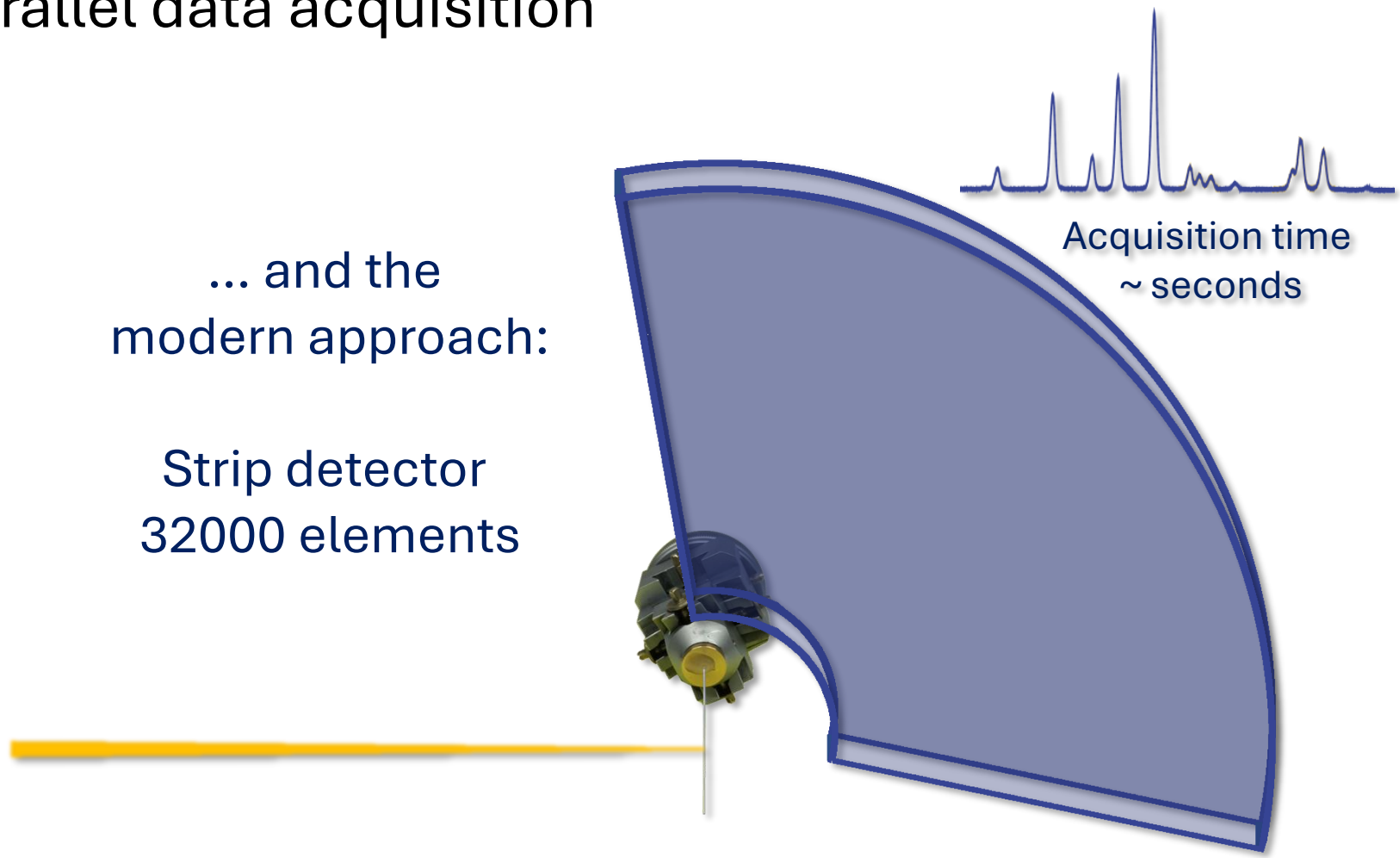
- Position sensitive detectors (Scanning)

Large stationary PSD

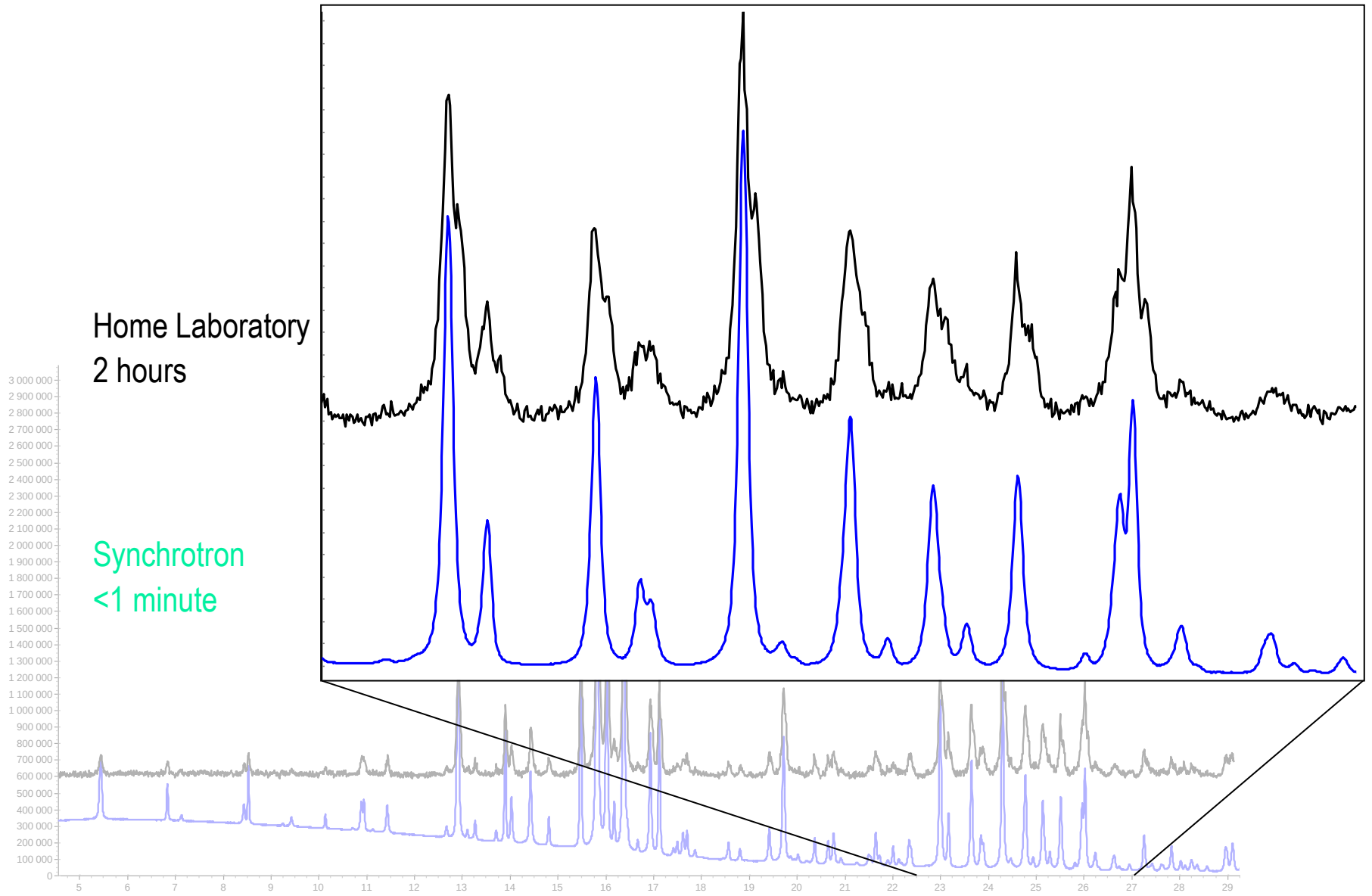
Parallel data acquisition

... and the
modern approach:

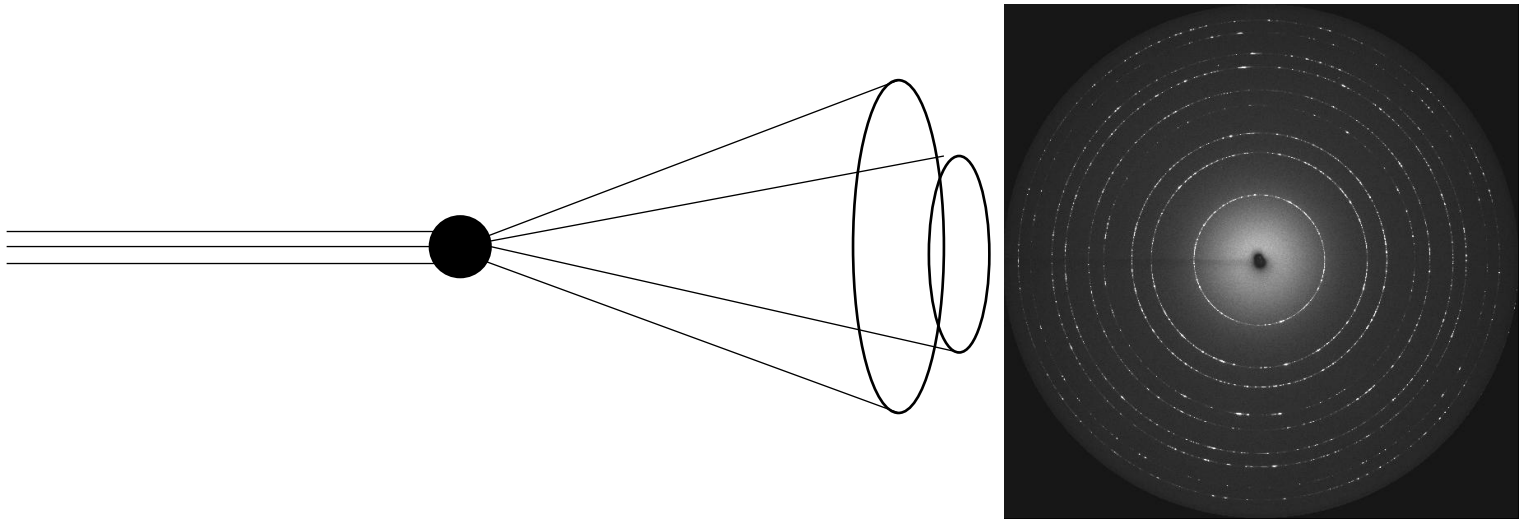
Strip detector
32000 elements



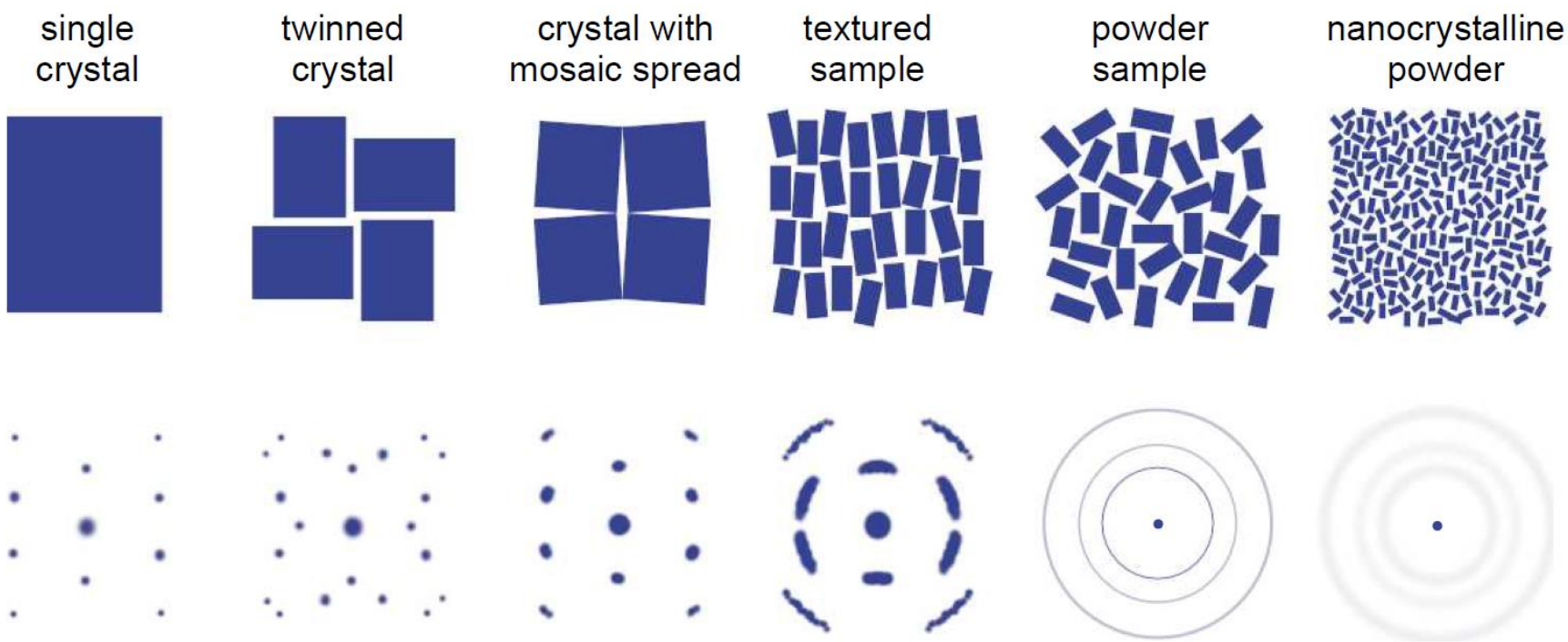
Powder diffraction with synchrotron radiation



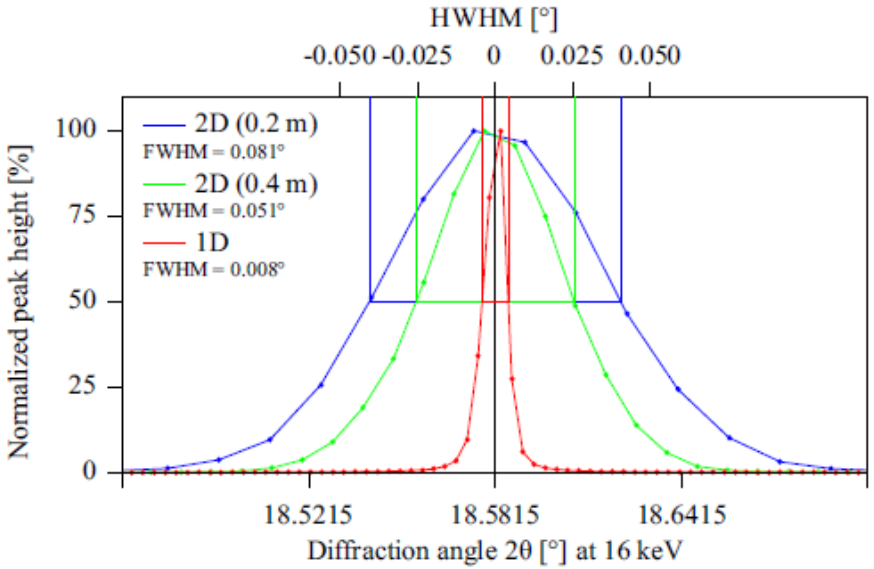
With Area detectors



We only usually take a slice!

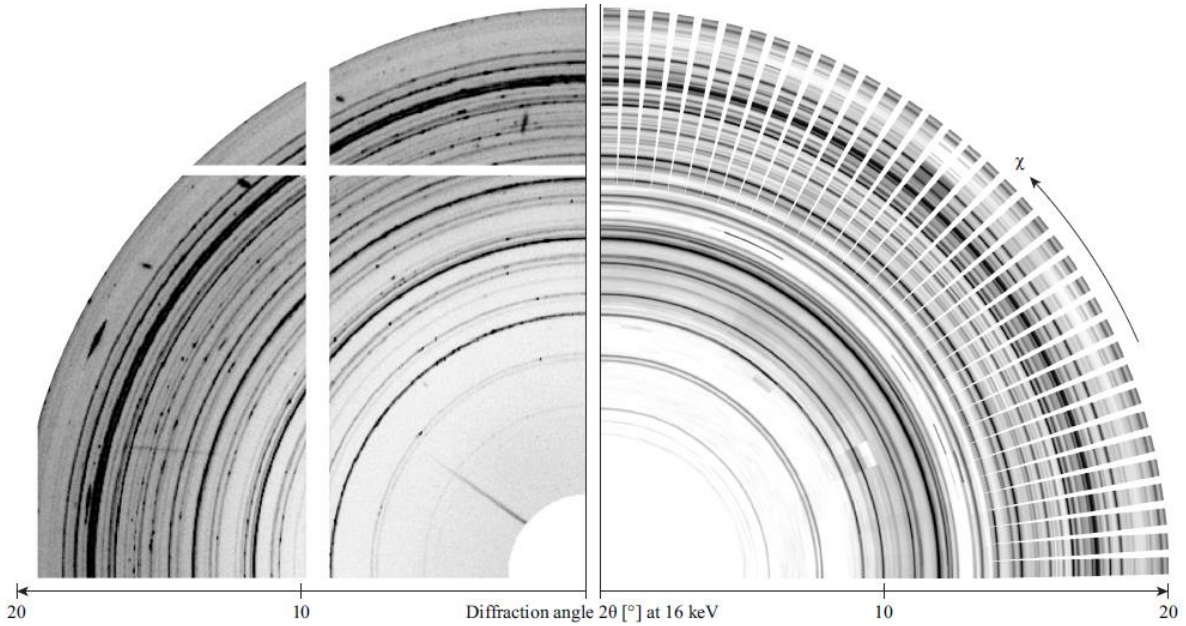


1D vs 2D

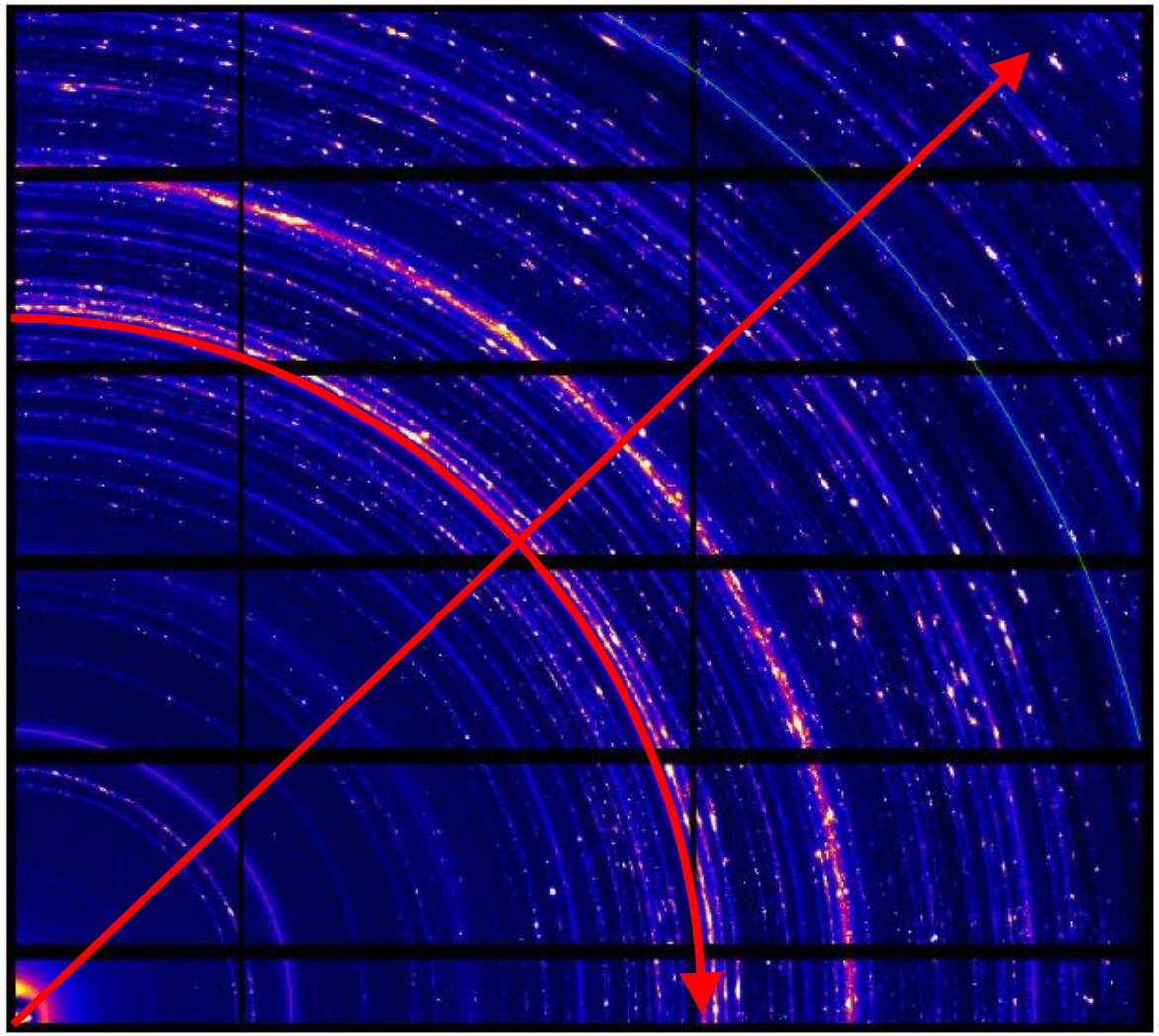


Resolution

Statistics



Non statistical powder

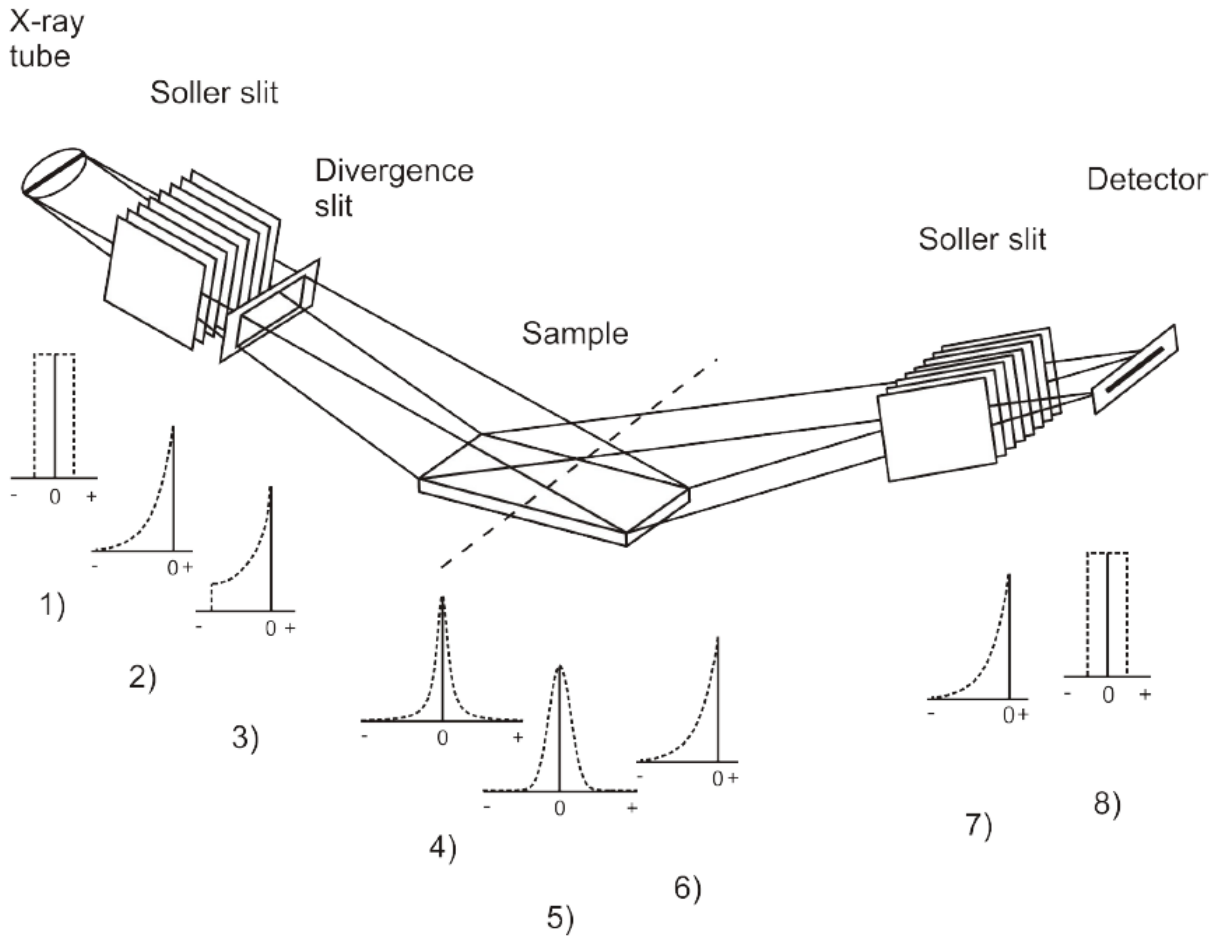


Too few grains due to

- Small amount of sample
- Small amount of a phase in a sample
- Impossibility to grind
- Impossibility to rotate/spin significantly the sample (chambers)
- On purpose oriented grains

Instrumental Resolution Function

Fundamental Parameters approach, each instrumental contribution is convoluted based on the known instrumental elements and contribution



Instrumental Resolution Function

Use of a calibrated standard (NIST SRM, CeO2, LaB6, Si etc.)

- Same exact setup needed if not internal
- Similar packing is external
- Similar absorption
- Similar or slightly extended angular range needed
- Should not contribute to the peak broadening

Fit the instrumental contribution as well as you can (Cauchy, Gaussians, Hats, various combinations, popular is the one by Caglioti, Paoletti, Ricci (1958))

Fix it

Analyse your sample. All remaining broadening comes from it

Peak broadening – Scherrer's

Exact for monodispersed, strain-free, cubic particles

In 1918 Scherrer devised the following:

$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$

- B is FWHM at 2θ
- K is 0.94 (for a cube)
- λ is the wavelength
- L is the **size**, bingo!

Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen.

Von

P. Scherrer.

Vorgelegt von P. Debye in der Sitzung vom 26. Juli 1918.

Über die innere Struktur der Kolloidteilchen ist bis jetzt mit Sicherheit nichts bekannt. Es ist daher interessant, typische anorganische und organische Kolloide nach der Methode der regellos orientierten Teilchen[1]) auf ihre Röntgeninterferenzen und damit auf ihren inneren Aufbau zu untersuchen. Es sind dabei von vorneherein zwei verschiedene Fälle denkbar.

1. Das einzelne Kolloidteilchen besitzt kristallinische Struktur. Dann haben wir auf unsern Röntgenaufnahmen zahlreiche Interferenzen zu erwarten, die in für das Raumgitter charakteristischer Weise angeordnet sind. Man hat sich natürlich zu überlegen, ob Kriställchen von der Größe von Kolloidteilchen noch Anlaß zu solchen Interferenzen geben können, ob nicht durch die Kleinheit der Teilchen die Erkennung der Kristallstruktur in Frage gestellt wird. Die Theorie gibt uns darüber folgende Aufschlüsse:

a) Die Lage der Interferenzen, die durch eine bestimmte kristallinische Substanz veranlaßt werden, hängt gar nicht von der Größe der verwendeten Einzelkriställchen ab. Sie ist ganz allein bestimmt durch die Art des Raumgitters.

b) Die Breite der Interferenzen hängt eng zusammen mit der Größe der verwendeten Einzelkriställchen, und zwar werden

1) P. Debye u. Scherrer, Phys. Z. 17, 277, 1916.

die Maxima um so breiter, je geringer die Anzahl der Elementarbereiche ist, die das Einzelteilchen umfaßt. Man ist sogar in der Lage durch Messung des Intensitätsverlaufs in den Interferenzen und damit der Breite derselben auf die Größe der verwendeten Kriställchen zu schließen, und bekommt damit, falls man es wirklich mit kristallinischen Teilchen zu tun hat, eine neue Methode zur Bestimmung der Teilchengröße. Die Theorie ergibt für die in bekannter Weise definierte Halbwertsbreite h des Maximums, das unter dem Winkel ϑ gegen den einfallenden Röntgenstrahl auftritt, den Wert:

$$h = 2\sqrt{\frac{\ln 2}{\pi}} \cdot \frac{\lambda}{\Delta} \cdot \frac{1}{\cos\vartheta/2}.$$

Dabei ist $\frac{\lambda}{\Delta}$ das Verhältnis der Wellenlänge der benutzten monochromatischen Röntgenstrahlen zur Kantenlänge des als würfelförmig vorausgesetzten Kriställchens.

2. Falls Kolloidteilchen keine kristallinische Struktur aufweisen, haben wir nur ein oder zwei sehr flache Maxima in der Nähe des einfallenden Röntgenstrahles zu erwarten[1]). Es ist dann schwer, Näheres über die innere Atomanordnung auszusagen.

Ausgehend von diesen theoretischen Überlegungen wurden Experimente angestellt die zu folgenden hauptsächlichen Resultaten führten:

1. Sie zeigten, daß kolloidale Au- und kolloidale Ag-Teilchen kleine Kriställchen darstellen, die genau dasselbe Raumgitter aufweisen wie makroskopische Goldkristalle. Es zeigte sich ferner die Formel für die Winkelabhängigkeit der Halbwertsbreite gut bestätigt und es ergaben sich für die Teilchengrößen Werte, die mit den auf anderen Wegen[2]) (Auszählung mit dem Ultramikroskop und osmotischer Druck) bestimmten Werten sehr gut übereinstimmten. Erwähnenswert ist, daß auch bei allerkleinsten Au-Teilchen, die nur noch 4—5 Elementarbereiche längs einer Würfelkante enthalten, also im Ultramikroskop längst nicht mehr sichtbar sind, das Raumgitter mit seinen charakteristischen Abständen genau erhalten bleibt.

2. Es wurden ferner gealterte Kieselsäure und Zinnsäure-Gele untersucht. Diese beiden vom kolloidchemischen Standpunkt so interessanten Körper zeigten neben den Anzeichen amorpher

1) P. Debye u. P. Scherrer, diese Zeitschr., Sitzung vom 17. Dez. 1915.
2) Herrn R. Zsigmondy bin ich für die Herstellung von Kolloiden, sowie für Bestimmung von Teilchengrößen zu Dank verpflichtet.

Körper intensive kristallinische Interferenzen. Wir haben es bei diesen Substanzen mit Körpern zu tun, die im Begriffe sind zu kristallisieren.

3. Typische organische Kolloide: Eiweiß, Gelatine, Kasein, Cellulose, Stärke usw. zeigten alle amorphe Struktur, eine Tatsache die es wahrscheinlich macht, daß diese Kolloidteilchen entweder Einzelmoleküle sind oder daß sie aus regellos nebeneinander gelagerten Molekülen bestehen.

Göttingen, Physikalisches Institut, 26. Juli 1918.

Peak broadening – Scherrer's

Exact for monodispersed, strain-free, cubic particles

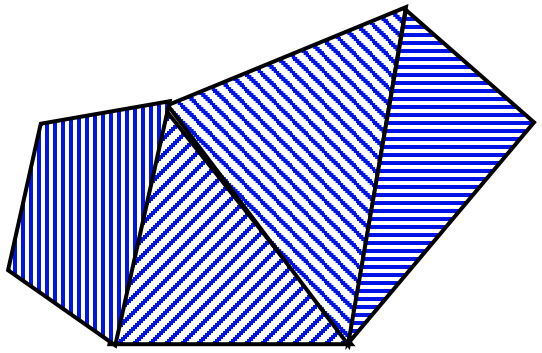
In 1918 Scherrer devised the following:

$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$

- B is FWHM at 2θ
- K is 0.94 (for a cube)
- λ is the wavelength
- L is the **size**, bingo!

Size of what?

- Crystallite (grain) – homogeneous diffracting portion
- Particles – agglomerates of 1 or more crystallites



Powder Diffraction is sensitive to crystallites, not particles

Peak broadening – Scherrer's

Exact for monodispersed, strain-free, cubic particles

In 1918 Scherrer devised the following:

$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$

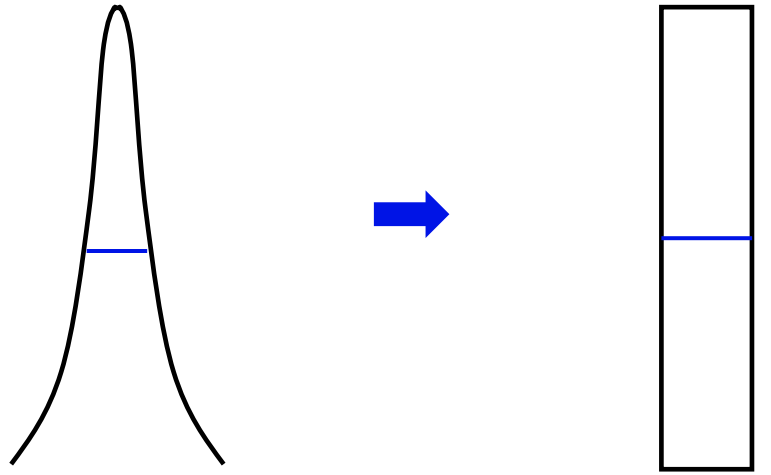
- B is FWHM at 2θ
- K is 0.94 (for a cube)
- λ is the wavelength
- L is the **size**, bingo!

Other shaped crystallites may have K values of different values.

It was noticed the Integral Breadth is less sensitive to particle shape and K ≈ 1

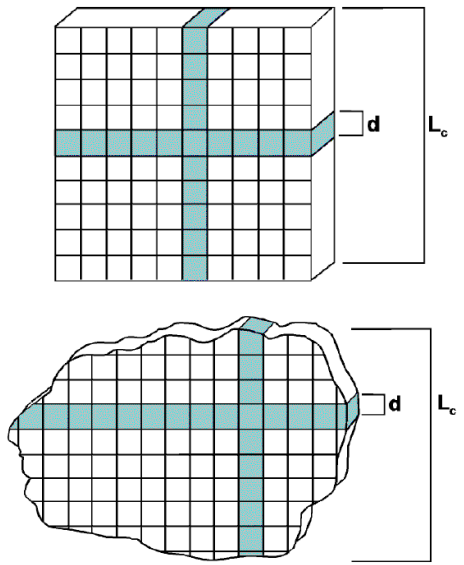
FWHM

IB: same area, same height
sensitive to integration

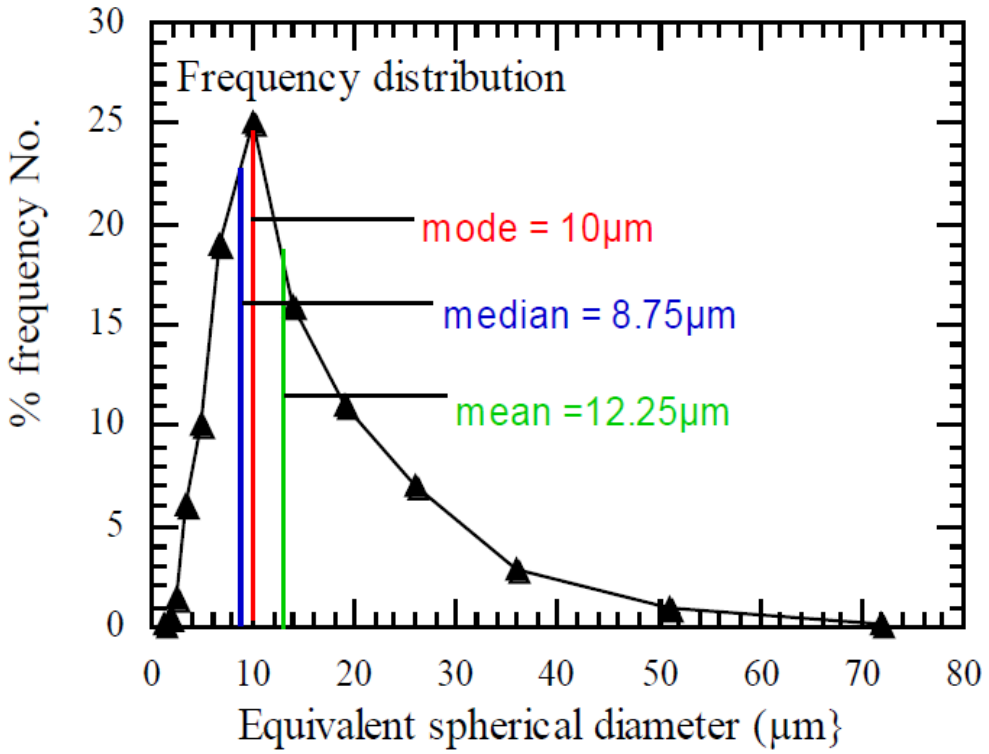


Which size?

- L_0 in Scherrer's formula is the edge of the cube
- L_{vol} is the volume weighted mean column length of a crystallite, defined in each direction
- Shape is needed to relate L_{vol} and L_0
- This is a single value, representing an entire size-distribution … inherently an approximation and one related to what diffraction 'sees' best. Shape is needed to get real numbers



Which size?



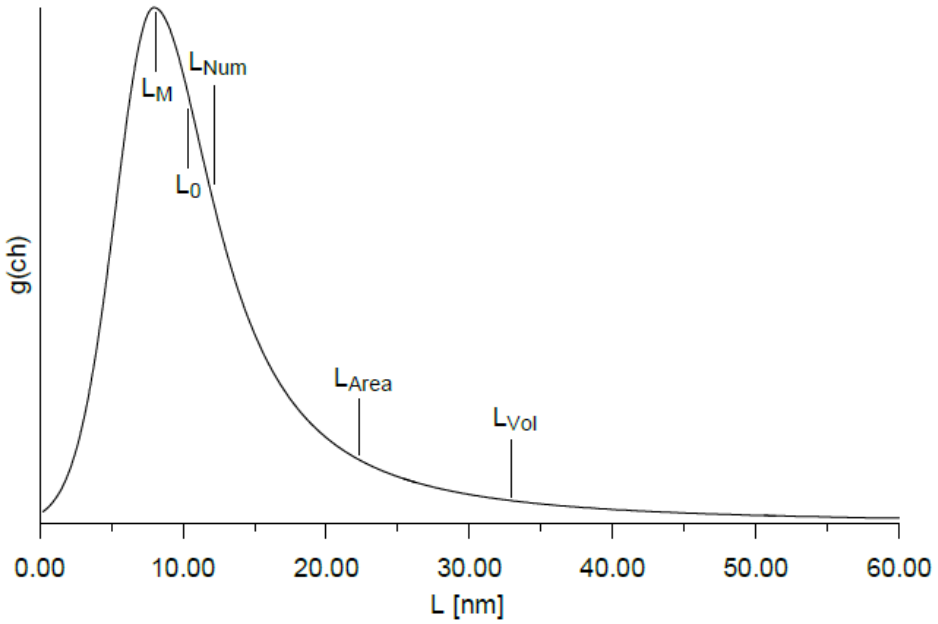
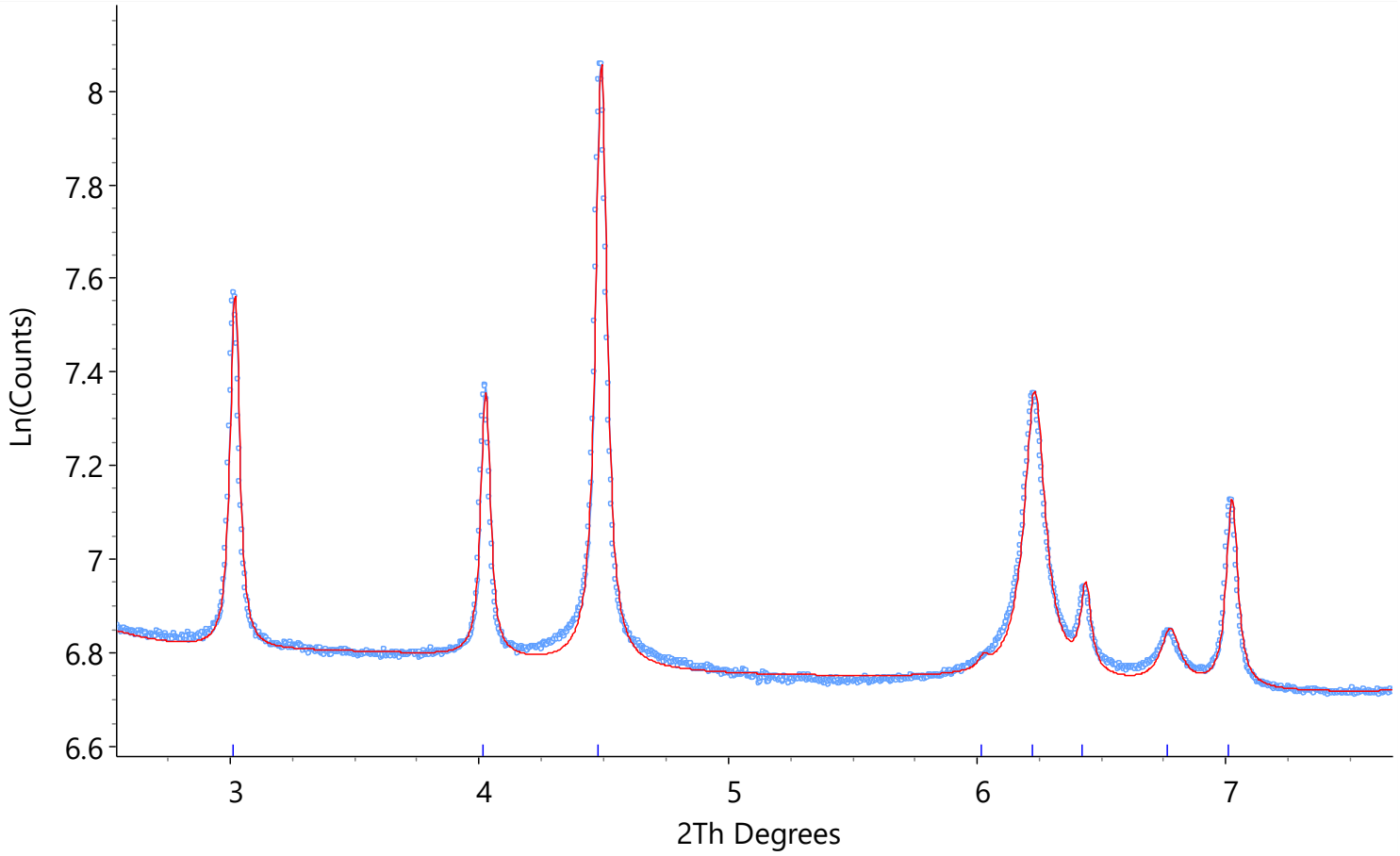


Fig. 7.4: Schematic representation of a column height distribution g(ch) showing the following characteristic points:

L_M : mode
L_0 : median
L_{Num} : number weighted mean
L_{Area} : area weighted mean
L_{Vol} : volume weighted mean

Anisotropic size broadening

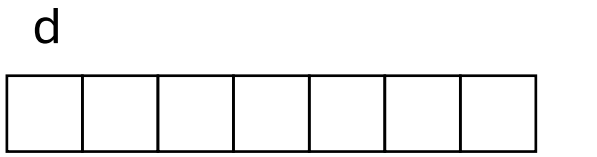


Moreover, anisotropic crystallites lead to anisotropic broadening, in this case the 111 peak is not well fitted

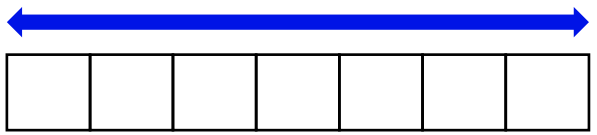
Anisotropic broadening is needed to improve materials understanding

Broadening – (micro)Strain

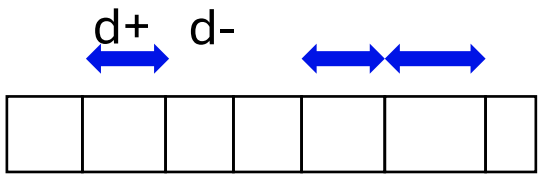
microstrain, often linked to defects, is representative of lattice distribution



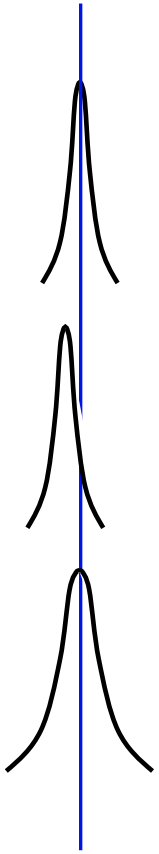
Pristine Crystal



Stressed Crystal



Microstrained Crystal



$B(\theta) = 4\varepsilon_0 \tan\theta \qquad \varepsilon_0 = \Delta d/d$

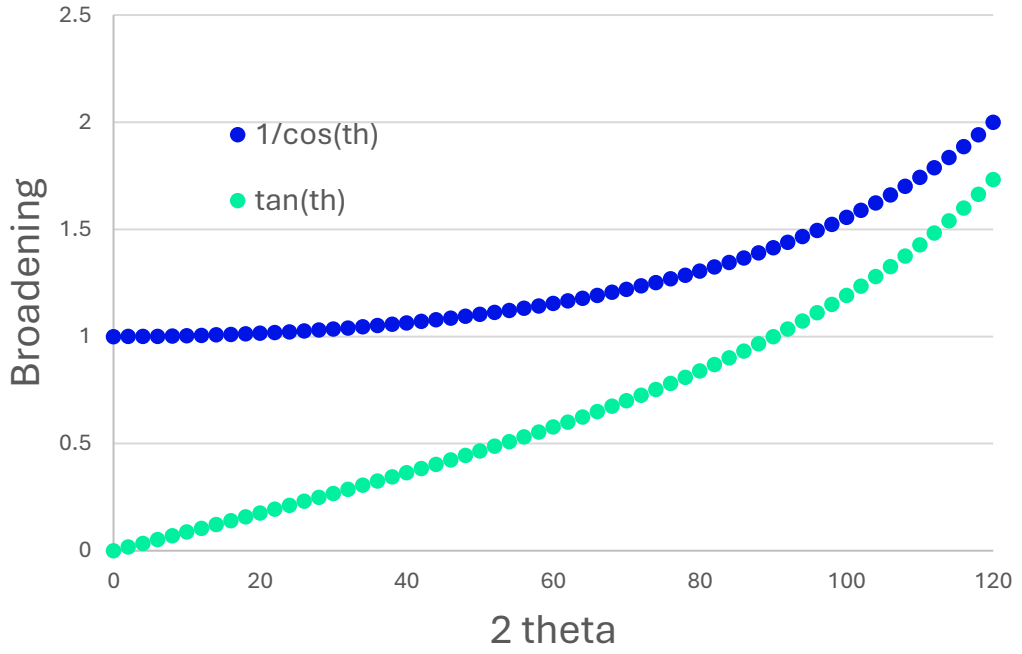
Broadening sources

Both size and microstrain cause a broadening that grows with angle, but with different dependencies, hence one could differentiate them (in principle …)

$B_L(\theta) = K \lambda / L_0 \cos\theta$

$B_\varepsilon(\theta) = 4\varepsilon_0 \tan\theta$

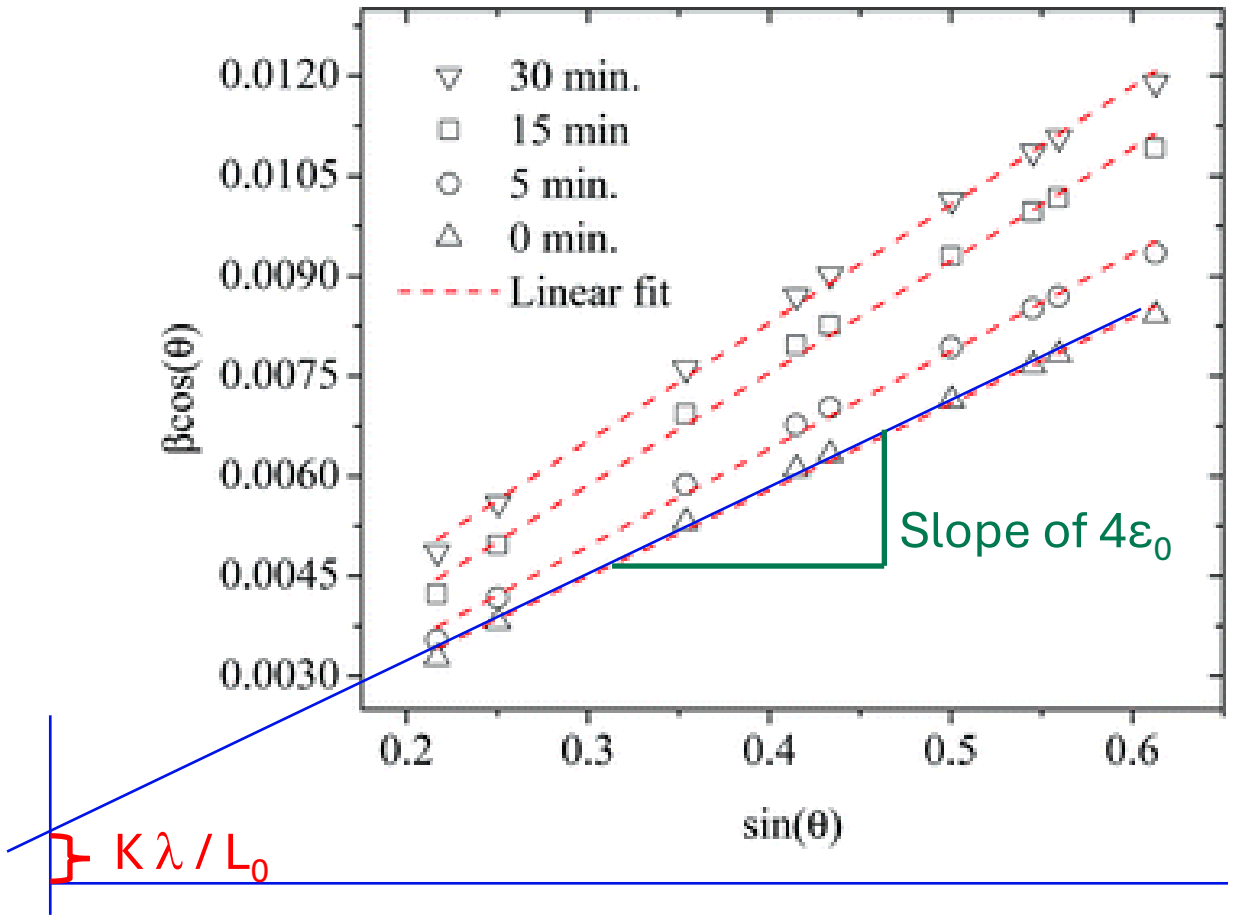
$B_{tot}(\theta) \cos\theta = 4\varepsilon_0 \sin\theta + K \lambda / L_0$



Williamson Hall plot

$B_{tot}(\theta) \cos \theta = 4\varepsilon_0 \sin\theta + K \lambda / L_0$

Things may turn a lot more complicated on less educated samples, with anisotropic broadening etc.



Microstrain sources

Table 1. The most typical correlations between diffraction peak aberrations, i.e. broadening, shifts or asymmetries, and the different elements of microstructure

Sources of strain	Peak aberrations				
	Peak shift	Peak broadening	Peak asymmetry	Anisotropic peak broadening	Peak shape
Dislocations		+	+	+	+
Stacking faults	+	+	+	+	+
Twinning	+	+	+	+	+
Microstresses		+			
Long-range internal stresses	+		+		
Grain boundaries	+	+			
Sub-boundaries	+	+			
Internal stresses	+				
Coherency strains	+	+	+		
Chemical heterogeneities	+	+	+		
Point defects					+
Precipitates and inclusions			+		+
Crystallite smallness		+		+	+

Can we get something good from refinements?

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Size–strain line-broadening analysis of the ceria round-robin sample

D. Balzar,[a,b]* N. Audebrand,[c] M. R. Daymond,[d] A. Fitch,[e] A. Hewat,[f] J. I. Langford,[g] A. Le Bail,[h] D. Louër,[c] O. Masson,[e] C. N. McCowan,[b] N. C. Popa,[i] P. W. Stephens[j] and B. H. Toby[k]

On a lognomal distribution of practically strain-free spherical CeO2 particles …

- Different instruments show similar results
- Different analytical methods show slightly dissimilar results
- Refinements are prone to fail if wrong strain and/or IRF is considered
- Pseudo-Voigt (or more complex) are required for correct interpretation

Can we get something good from refinements?

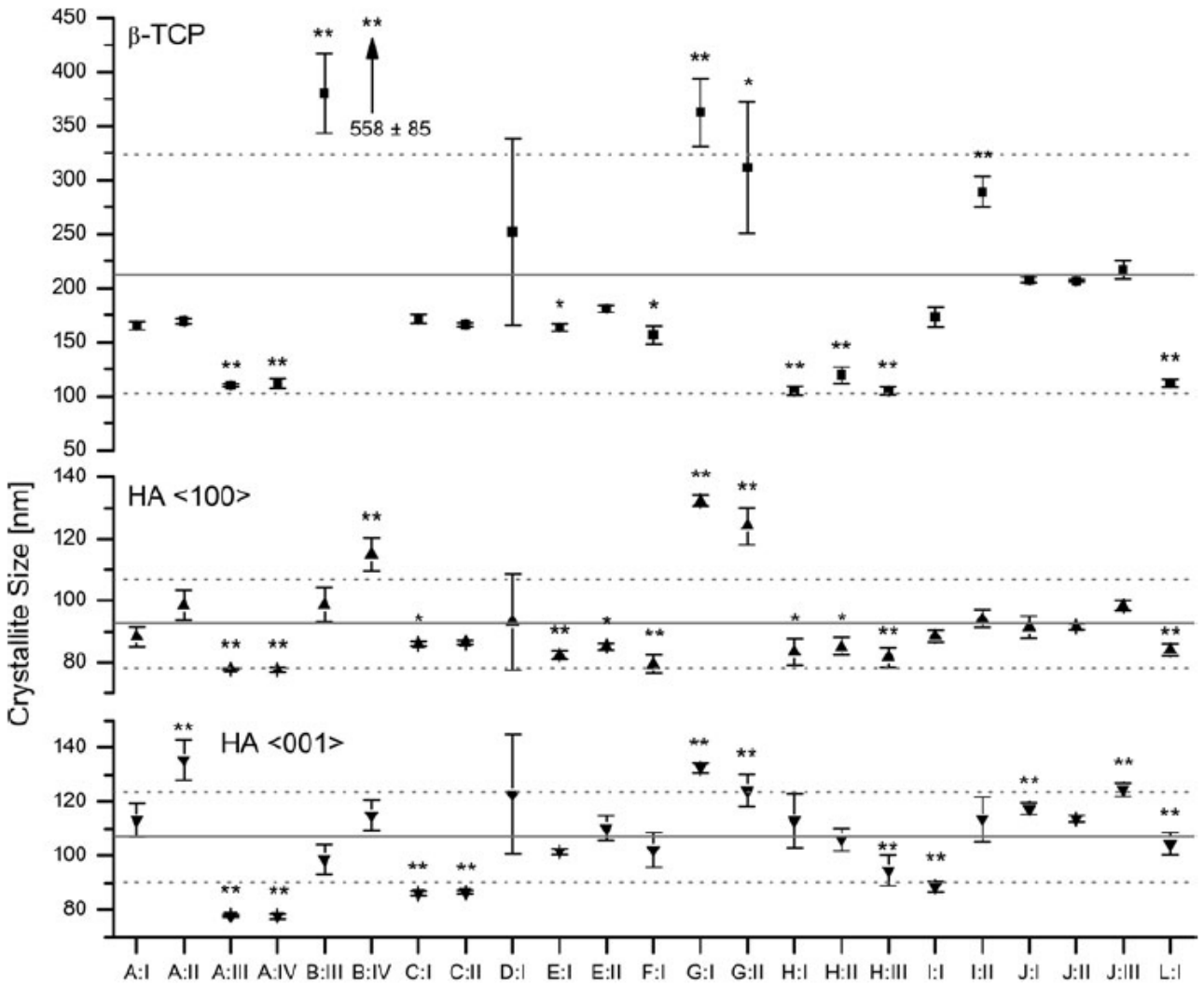
Interlaboratory study on the quantification of calcium phosphate phases by Rietveld refinement

Nicola Döbelin[a)]
RMS Foundation, Bischmattstrasse 12, 2544 Bettlach, Switzerlan

(Received 25 November 2014; accepted 17 April 2015)

[doi:10.1017/S088571561500038X]

Initially meant for quantification but including sample size and lattice



A bit more advanced, WPPM

Acta Crystallographica Section A
Foundations of Crystallography
ISSN 0108-7673

Received 16 October 2001
Accepted 11 December 2001

Whole powder pattern modelling

P. Scardi* and M. Leoni

Dipartimento di Ingegneria dei Materiali, Università di Trento, 38050 Mesiano (TN), Italy.
Correspondence e-mail: paolo.scardi@ing.unitn.it

Does not compute arbitrary shape functions for peaks but rather analytical contributions based on the different effects of shape and size distribution, dislocations, stacking faults, grain surface relaxation etc.
Incidentally can also include the structure …
As for every refinement, results are as good as the educated assumptions that guide the choice of parameters

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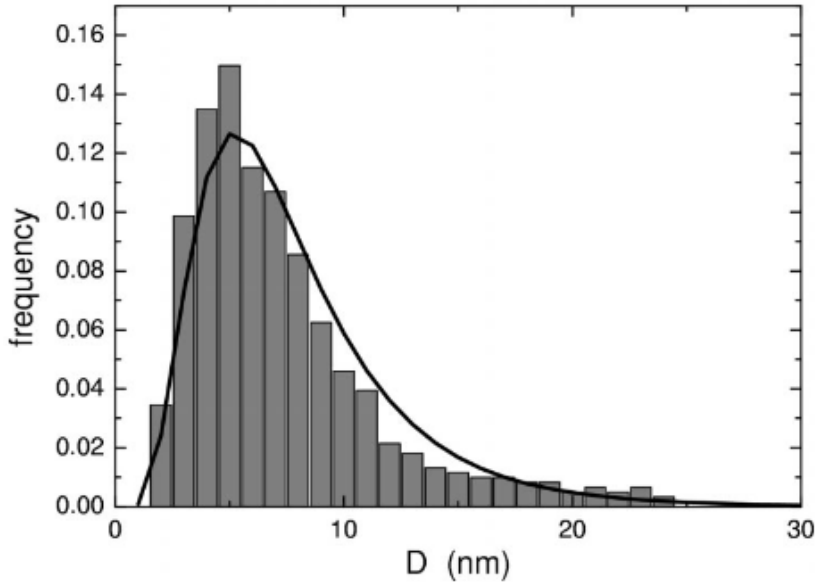
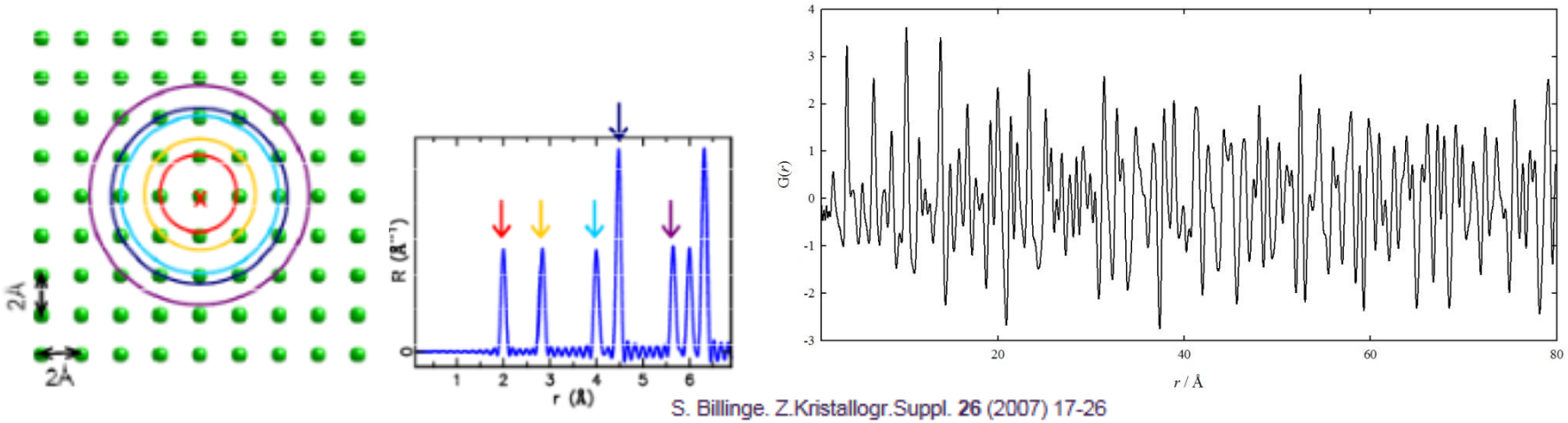


Figure 6
Grain-size distribution for sample 96 h: TEM (histogram) and WPPM result (line).

Total scattering, the Pair Distribution Function



S. Billinge. Z.Kristallogr.Suppl. **26** (2007) 17-26

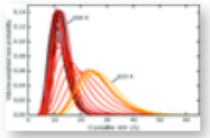
Computed from the FT of the **entire** pattern, represents the probability distribution of finding electron density (i.e. an atom) at a given distance r from another

Requires high energy to reach very high Q values as in principles requires ALL diffraction

Suitable also for amorphous, liquid and nanocrystalline

Total scattering, the Pair Distribution Function

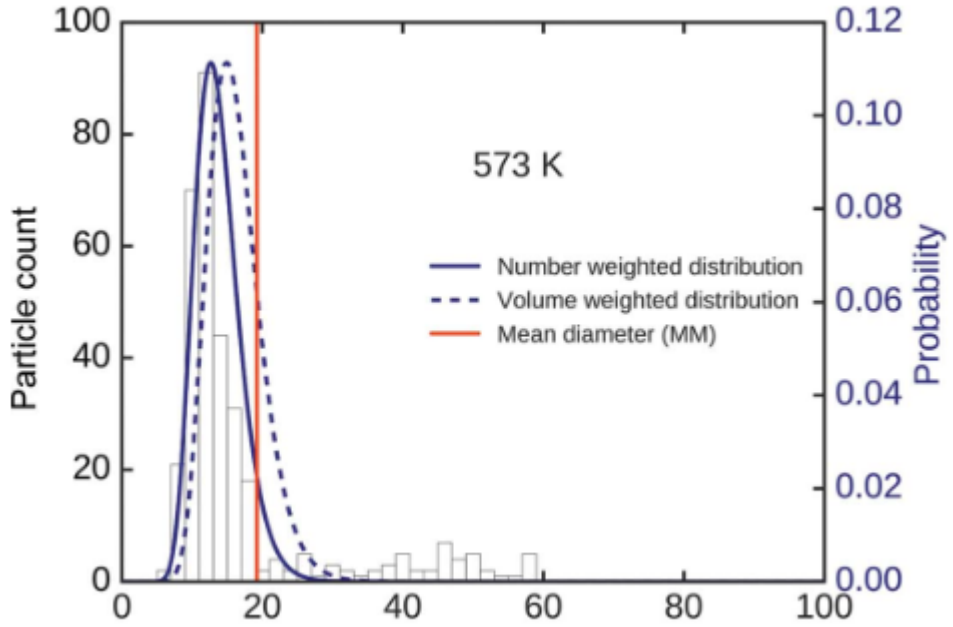
RESEARCH PAPERS
J. Appl. Cryst. (2017). **50**, 741-748
https://doi.org/10.1107/S1600576717003715
Cited by 37

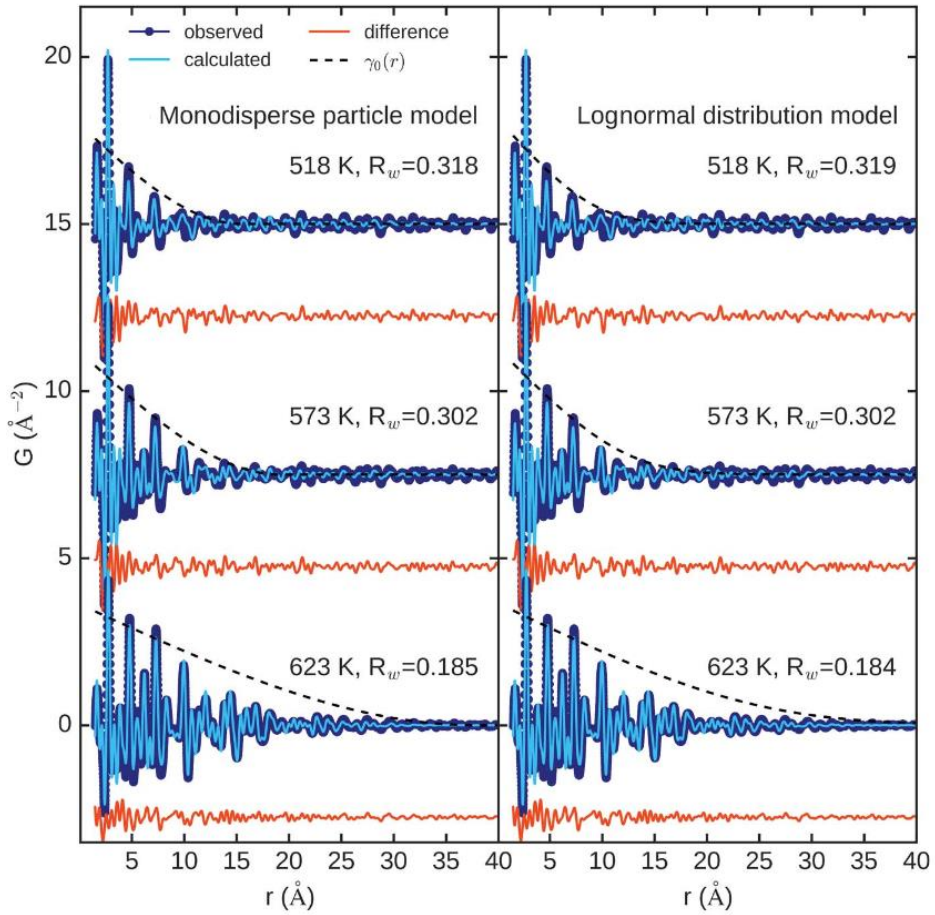


Modelling and validation of particle size distributions of supported nanoparticles using the pair distribution function technique

L. Gamez-Mendoza, M. W. Terban, S. J. L. Billinge and M. Martinez-Inesta

A monodispersed and a Lognormal model were fitted to the data





The Debye Scherrer Equation

- Calculates the intensity at a given q as the sum of all pairwise contributions from atom pairs
- Same approach as PDF but works in reciprocal space and describes analytically (does not need) the total wide-angle scattering
- Requires a sensible model
- Computational wise choices to be made, works better for NP as less atoms!
- Can incorporate naturally size, shape, defects etc.

$$I(q) = \sum_{i=1}^{N} \sum_{j=1}^{N} f_i f_j \frac{\sin(q r_{ij})}{q r_{ij}}$$

The Debye Scherrer Equation

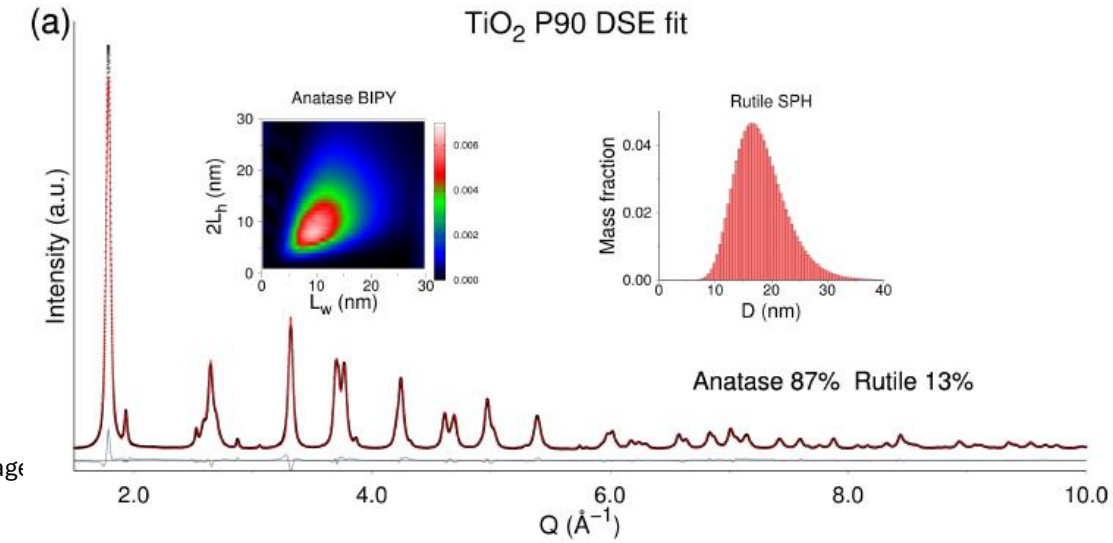
nanomaterials

Article

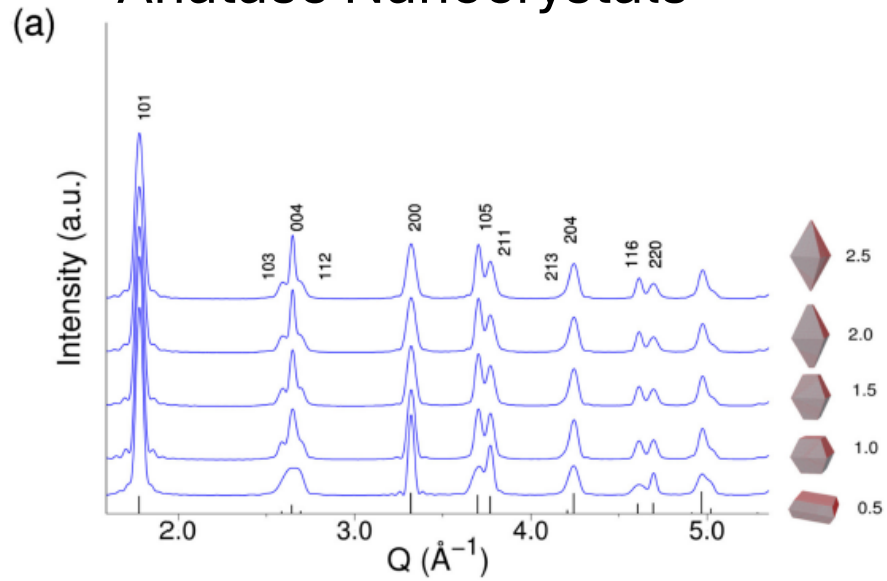
Structure, Morphology, and Faceting of TiO_2 Photocatalysts by the Debye Scattering Equation Method. The P25 and P90 Cases of Study

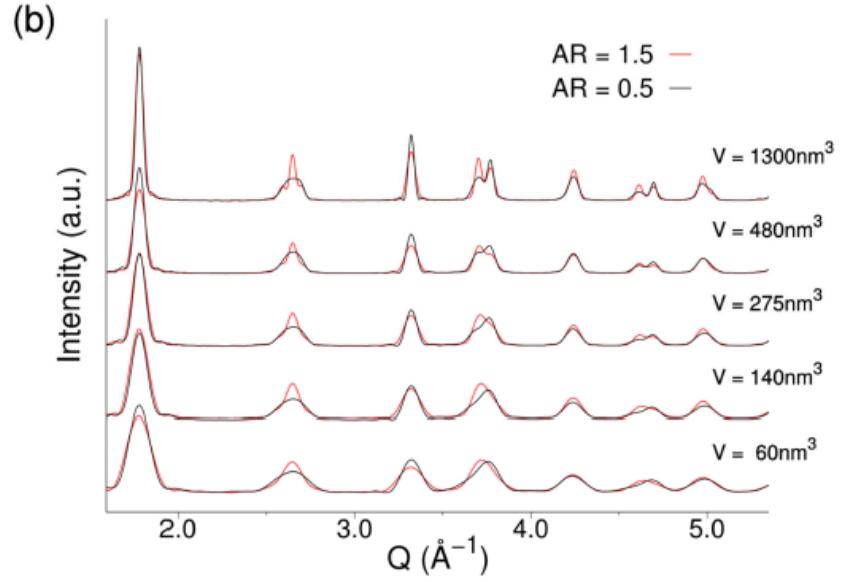
Federica Bertolotti [1,*], Anna Vivani [1], Daniele Moscheni [1], Fabio Ferri [1], Antonio Cervellino [2], Norberto Masciocchi [1,*] and Antonietta Guagliardi [3,*]

Refinement on a commercial sample of a bivariate population of bipyramidal shapes



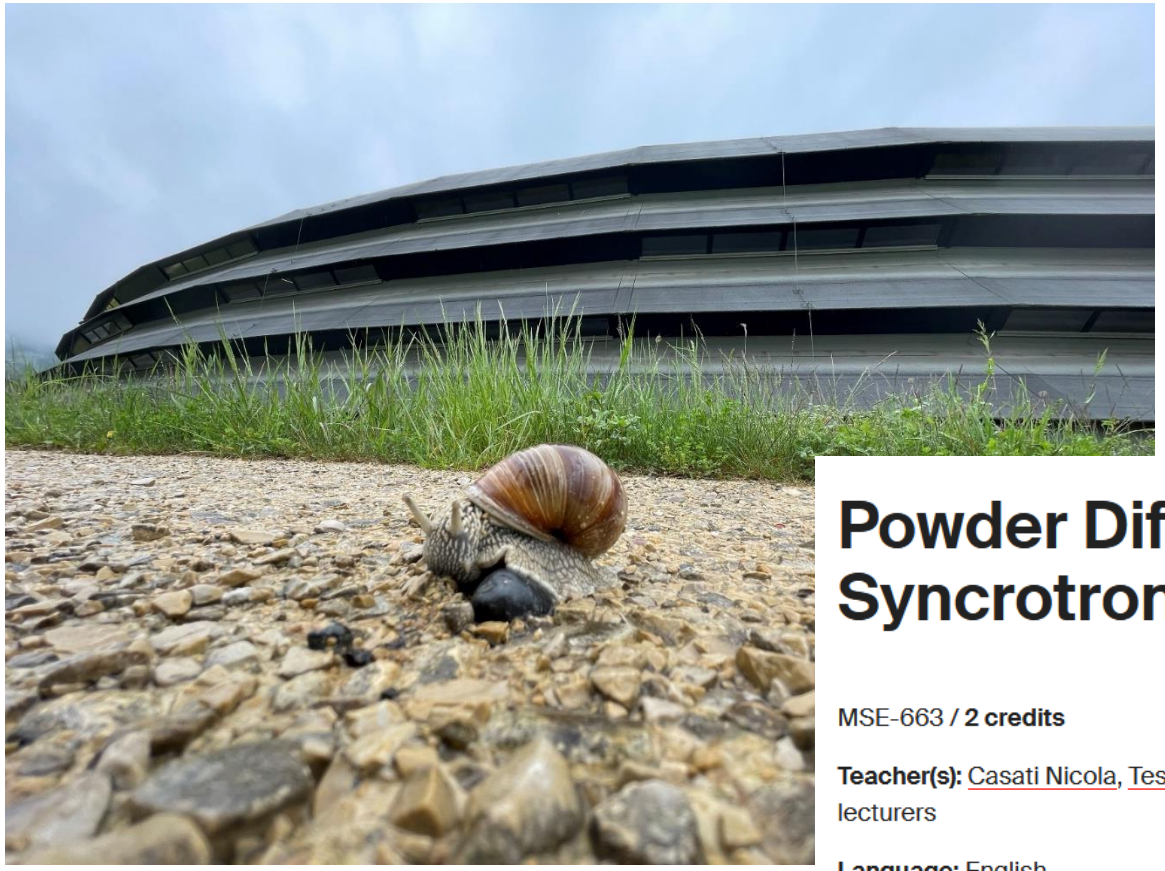
Anatase Nanocrystals





See you at SLS-2!

PSI



Powder Diffraction School - Modern Syncrotron Methods

Download the coursebook (PDF)

MSE-663 / **2 credits**

Teacher(s): Casati Nicola, Testino Andrea, Van Petegem Steven, Various lecturers

Language: English

Remark: Next time: 2025

Frequency

Every 2 years

In the programs

Materials Science and Engineering
2024-2025 Doctoral School

- **Number of places:** 40
- **Exam form:** Oral (session free)
- **Subject examined:** Powder Diffraction School - Modern Syncrotron Methods
- **Courses:** 23 Hour(s)
- **Exercises:** 9 Hour(s)
- **TP:** 2 Hour(s)
- **Type:** optional

What's a refinement?

You have data

Criteria of fit	Definition
"R-pattern", R_p	$R_p = \frac{\sum \lvert Y_{o,m} - Y_{c,m} \rvert}{\sum Y_{o,m}}$
"R-pattern", R_p' (background corrected)	$R_p' = \frac{\sum \lvert Y_{o,m} - Y_{c,m} \rvert}{\sum \lvert Y_{o,m} - Bkg_m \rvert}$
"R-weighted pattern", R_{WP}	$R_{wp} = \sqrt{\frac{\sum w_m (Y_{o,m} - Y_{c,m})^2}{\sum w_m Y_{o,m}^2}}$
"R-weighted pattern", R_{WP}', (background corrected)	$R_{wp}' = \sqrt{\frac{\sum w_m (Y_{o,m} - Y_{c,m})^2}{\sum w_m (Y_{o,m} - Bkg_m)^2}}$
"R-expected", R_{exp}	$R_{exp} = \sqrt{\frac{M-P}{\sum w_m Y_{o,m}^2}}$
"R-expected", R_{exp}' (background corrected)	$R_{exp}' = \sqrt{\frac{M-P}{\sum w_m (Y_{o,m} - Bkg_m)^2}}$
"Goodness of fit", GOF	$GOF = chi = \frac{R_{wp}}{R_{exp}} = \sqrt{\frac{\sum w_m (Y_{o,m} - Y_{c,m})^2}{M-P}}$
"R-Bragg", R_B	$R_B = \frac{\sum \lvert I_{"o",k} - I_{c,k} \rvert}{\sum I_{"o",k}}$